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SPONTANEOUS IGNITION AND CHAIN REACTIONS†

N. N. Semenov

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I. INTRODUCTION

Our work in the field of chemical kinetics was begun about 1924 in the Electronic Chemistry Laboratory which I at that time directed in the Leningrad Physicotechnical Institute. My first coworkers were Kondrat'ev and Khariton, who were then quite young, and are now Academicians. Our group of physicists was augmented with young people and by the nineteen-thirties it had grown into the fairly large group of the Chemical Physics Institute of the Academy of Sciences of the USSR.

In 1925 we were concerned with the problem of the spontaneous ignition of gases capable of undergoing combustion and exploding. From the viewpoint of chemical kinetics, this problem was almost untouched. In any case it had never been the centre of a research effort. This situation was probably responsible for our rapid progress. In a period of 5–7 years we laid the foundations of the theory of spontaneous ignition and established that there are two and only two types of spontaneous ignition, namely: (1) thermal spontaneous ignition; and (2) chain spontaneous ignition (branched chain reactions).

I believe that this is the most important result which I and my closest associates achieved in the course of my long life.

Thermal spontaneous ignition results from the liberation of heat in exothermic reactions and the production of a thermal avalanche, since the heat liberated, and hence the increase in the temperature of the gas, leads to an increase in the reaction rate, which in turn leads to an increase in the liberation of heat and to a further increase in temperature, and so on.

Chain spontaneous ignition also results from the liberation of energy in chemical reactions, not in the form of heat, but at a stage before the energy is converted into heat. This energy being liberated leads to an increase in the number of free atoms, radicals, and electronically-excited particles with extremely high chemical activity, that is, to the development of a so-called chain avalanche. Here the increase in the temperature of the gas is a result, and not the cause, of the spontaneous ignition.

All subsequent studies in this country and abroad confirmed these conclusions, not only qualitatively, but quantitatively. Even when nuclear explosions were discovered, they were also found to be of the same two types — thermonuclear and branched-chain. Formally, the theories were also found to be similar, although they naturally differed quantitatively.

II. THERMAL SPONTANEOUS IGNITION

The earliest work (on thermal explosion) began with the development of a quantitative theory, which was subsequently verified by experiment. The history of our development of the thermal theory of explosion is extremely

† This review is based on a paper presented at the Symposium on Chain and Radical Reactions on the 11th April 1966 in the Scientists' Club, Moscow.

curious. In addition to our early work on chemical kinetics in 1923–1926, Val'ter and I were concerned with the problem of the breakdown of dielectrics. As a result of this work[1,2], we formulated the thermal theory of breakdown due to the breakdown of thermal equilibrium between the Joule heat being liberated and the heat removed from the body of the dielectric to the electrodes.

The fortunate idea that all the conclusions from the thermal theory of breakdown were applicable to the theory of spontaneous ignition or — which is the same thing — spontaneous explosion, came to us in 1927. Here the liberation of heat was associated with a chemical reaction, albeit a very slow one: $Q_1 = q_1 W$, where q_1 is the heat of reaction and W the reaction rate calculated for the entire volume of the vessel v. Thus $W = vw$, where w is the reaction rate in unit volume. In the simplest example $w = k_0 a^n e^{-E/RT}$, where k_0 is the pre-exponential term of the reaction rate constant, E the activation energy, $n = 1$ for unimolecular reactions and $n = 2$ for bimolecular reactions, and a the number of parent molecules per unit volume (if w is expressed as the number of molecules which have reacted in unit time). Thus the quantity Q_1 increases rapidly with the initial temperature of the gas T_0 according to the exponential $e^{-E/RT}$ law. The heat transfer Q_2 takes place through the walls of the vessel. For convective heat transfer we have $Q_2 = \kappa(T - T_0)s$, where T is the temperature of the gas being heated by the reaction, T_0 the temperature of the walls, and s the surface area of the vessel. The form of the expression is the same for conductive heat transfer.

Let us plot Q_1 and Q_2 as functions of temperature on the same diagram. Let us consider the example where p is constant and T_0 is variable (Fig. 1) and that where T_0 is constant and p is variable (Fig. 2). Curves *1* in both diagrams correspond to thermal equilibrium with an increase in the temperature of the gas by the small quantity ΔT. Curves *3* in both figures, for which Q_2 is always less than Q_1, correspond to there being no thermal equilibrium, that is, to the production of a thermal avalanche leading to spontaneous explosion. Curves *2*, for which the heat-transfer straight line touches the heat-production curve, separate the two regions and determine in Fig. 2 the ignition temperature T_0 at a given pressure or in Fig. 1 the ignition pressure at a given temperature T_0. At the point of tangency $Q_1 = Q_2$ and $\frac{dQ_1}{dT} = \frac{dQ_2}{dT}$.

By solving these equations, we obtain the critical condition for explosion:

$$\delta_{cr} = \frac{qvk_0 a^n Ee}{NRT_0^2 \kappa s} e^{-E/RT_0} = 1, \qquad (1)$$

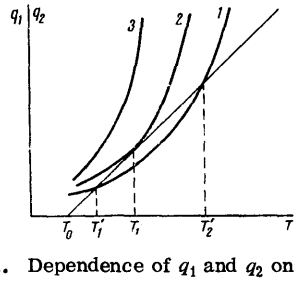


Fig. 1. Dependence of q_1 and q_2 on T (see text for explanation).

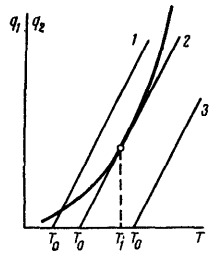


Fig. 2. Dependence of q_1 and q_2 on T (see text for explanation).

where a is expressed as the number of molecules per unit volume, and q is the molar heat of reaction.

If $\delta_{cr} \geqslant 1$, explosion will always take place, and if $\delta_{cr} \leqslant 1$, no explosion will take place.

Since $a \simeq 10^{19}(p/T)$, we can write the equation

$$\delta_{cr} = \frac{qk_0 Eevp^n \times 10^{19}}{NR\kappa s T_0^{2+n}} e^{-E/RT_0} = 1. \qquad (2)$$

For a given vessel and a given heat-transfer coefficient κ, we obtain the following relationship between the critical values of T_0 and p:

$$\log \frac{p}{T_0^{1+2/n}} = \frac{A}{T_0} + B. \qquad (2')$$

The constant B is determined by the kinetic and thermal constants and by the shape and dimensions of the vessel, and the quantity $A = 0.217E/n$. The theory was formulated in this form in my paper[3,4] in 1928. In the same year our colleague Zagulin published a paper[5] in which it was shown for the example of the spontaneous ignition of Cl_2O, that formula (2′) is confirmed experimentally.

From earlier kinetic experiments, carried out abroad, it was known that the decomposition of Cl_2O takes place by a bimolecular reaction with activation energy $E \simeq 25\,000$ cal × × mole^{-1}. Knowing the value of A, Zagulin was able to determine the value of E from explosion experiments, and in this way he obtained the same value $E = 25\,000$ cal mole^{-1}.

In 1935 Rice and Allen[6] obtained analogous verification for the example of the decomposition of azomethane. From kinetic data it was established that the reaction is unimolecular and has an activation energy of 51 000 cal mole^{-1}. In a study of the spontaneous ignition of azomethane, Rice and Allen confirmed the correctness of formula (2′) and from the value of A they found the activation energy E to be 50 000 cal mole^{-1}, in excellent agreement with the kinetic data.

These experiments convinced everyone that the thermal theory correctly takes account of the part played by kinetics in spontaneous-ignition processes. For complete confidence, however, it was necessary to show that, from a knowledge of the kinetic and thermal parameters, we were able, by applying the theory of thermal explosion, to calculate theoretically the ignition temperature for various gas pressures. This was achieved in our Institute by Frank-Kamenetskii[7], who examined the case of conductive heat transfer in a cylindrical vessel. The only change in the value of the critical parameter δ_{cr} in this example is that in

formula (2) the coefficient κ is replaced by $4\lambda/r$ and $v/s = r/2$. Substituting the values of λ, r, E, and q, Frank-Kamenetskii calculated the spontaneous-ignition temperatures of azomethane, methyl nitrite, and dinitrogen monoxide at various pressures. The calculated values were found to be very close to the experimentally determined spontaneous-ignition temperatures. This confirmed conclusively the quantitative reliability of the thermal theory of explosion[8].

Thermal explosion will always take place if $\delta_{cr} \geq 1$; this can be written in the form

$$t_r \leqslant \frac{qEet_e}{CRT_0^2}, \qquad (3)$$

where t_e is the thermal relaxation time of the system, that is, the time required to cool by a factor of e a gas heated by the reaction, C the heat capacity of the gas, and t_r the duration of the reaction, an arbitrary quantity which can be readily determined by measuring the initial reaction rate

$$t_r = \frac{d}{k_0 a^n e^{-E/RT}}, \qquad (4)$$

where a is the number of molecules per unit volume for the original fuel gas. If $t_r \geqslant \frac{qEet_e}{CRT_0^2}$, thermal ignition is impossible. If $t_r \leqslant \frac{qEet_e}{CRT_0^2}$, the fuel gas is always ignited thermally. The time t_r for a given gas pressure, that is, for a given number of molecules a in unit volume, is inversely proportional to the reaction rate close to the explosion temperature. Thus in order to determine whether an explosion is thermal in character, it is sufficient to measure the initial reaction rate at a pressure only just less than the explosion pressure, to measure or calculate the relaxation time t_e, and to estimate, even approximately, the value of the activation energy E. If the reaction rate corresponds even approximately to the expression (3), the explosion is undoubtedly thermal in character. If, however, t_r is found to be greater by one or several orders of magnitude, this is a reliable indication that the ignition is not thermal in character but is a chain process.

Until now we have restricted ourselves to simple unimolecular and bimolecular reactions. The theory can readily be generalised to more complicated kinetic laws, for example to autocatalytic reactions, chain reactions with unbranched chains, etc. The problem here reduces basically to the problem of making allowance for the more complicated kinetic laws.

We also studied experimentally the problem of the course of a thermal explosion with time. It was found that thermal explosion does not take place instantaneously, but after a certain induction period (usually of the order of one second or fractions of a second for non-autocatalytic reactions). The problem was developed theoretically by Todes[9,10], in complete agreement with experiment. This examination showed that the temperature of pre-ignition heating $\Delta T = \frac{RT_0^2}{E}$ is reached comparatively slowly, but that explosion takes place almost instantaneously when this temperature has been reached. When the thermal spontaneous-ignition temperature or pressure are much greater than the critical values and we can neglect heat transfer, we obtain from theory, for the induction period t_i, the expression $t_i = t_r \frac{CRT_0^2}{Eq}$, in good agreement with experiment.

Let us now consider the idealised case of a purely adiabatic thermal explosion, in which the heat transfer is equal to zero, and $t_e = \infty$. It can readily be seen from the criterion that thermal explosion is possible at any value of t_r, no matter how great, or, which is the same thing, at any values of the reaction rate, no matter how small. We have seen from the previous formula, however, that the induction period will then reach improbably high values. Thus if for a given fuel gas with E = 40 kcal mole^{-1} at a temperature T_0 = 600°K the induction period t_i is equal to 1 s, the value of t_i at T_2 = 300°K will be greater by a factor of $\exp\left[\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$, that is, the time required for thermal explosion to take place reaches millions of years. This is of course, the same result as if the explosion were impossible. If, however, the temperature is not 300° but 450°K the induction period will be equal to 14 h. The problems of predicting long induction periods for long relaxation times, particularly in the case of solid explosives, is of some practical importance. It should be noted that under given conditions these extremely long induction periods in practice retain their very precise value.

It should be noted that up to the mid nineteen-twenties the problems of spontaneous ignition and flame propagation had been examined by explosives experts, heat engineers, and to some extent by physicists and mechanical engineers. Since the time of van't Hoff, these problems had been of little interest to physical chemists. As a rule, no account was taken of chemical kinetics in problems of combustion. In its place there was introduced the concept of spontaneous-ignition temperature as a constant characteristic of each fuel. We have shown above that the spontaneous-ignition temperature is not a constant quantity. In our work, the phenomenon of combustion was based on chemical kinetics, complicated by the liberation of heat and by the existence of an inverse relationship between increase in temperature and kinetics. This was the first instance of a wider class of phenomena, now known as macrokinetics. It was on this basis that it was subsequently possible to convert not only the theory of spontaneous ignition but also the theory of various forms of flame propagation into a chapter of chemical kinetics. This principle subsequently formed the basis for the theory of flame propagation (B. Lewis, Ya. B. Zel'dovich, D. A. Frank-Kamenetskii, N. N. Semenov, and others), the concentration limits of the ignition and propagation of a normal flame (Zel'dovich), some problems of turbulent flame propagation (in particular K. I. Shchelkin), problems of the concentration limits of the detonation and combustion of powders (A. F. Belyaev and O. I. Leipunskii), etc. In recent years we have developed a theory of the spontaneous ignition of condensed explosives.

III. CHAIN SPONTANEOUS IGNITION

In contrast to thermal spontaneous ignition, the work here began not from theory but from experiment. In 1926, Khariton[11], who was occupied with problems of the extinction of the chemiluminescence of phosphorus vapour at low oxygen pressures, unexpectedly discovered that at a certain fairly low oxygen pressure, below a limiting pressure p_1, phosphorus vapour did not ignite. The vapour pressure of phosphorus (over a piece of phosphorus in a vessel at room temperature) and oxygen was so low (0.1–0.001 mmHg depending on the conditions of the experiment) that there could be no question of thermal ignition. This was also proved by direct experiment.

Moreover, phosphorus vapour undergoing combustion at $p > p_1$ is extinguished immediately as soon as the oxygen pressure falls, as a result of the oxidation of phosphorus, to a pressure only just less than p_1, although the apparatus still contains oxygen and phosphorus. If a certain quantity of inert gas (argon) is added at $p < p_1$, a flash is produced. Thus the limiting value of the partial pressure of oxygen p_1 is for some reason decreased in the presence of argon.

These observations radically contradicted the theories held at that time, since the rate of a reaction always decreases smoothly as the components are consumed, and there seemed to be no reason for the reaction to stop suddenly.

The extent to which these results of ours appeared paradoxical at that time can be seen from the criticism of the famous scientist Bodenstein [12], who was the leader in world chemical kinetics at that time. He wrote that Khariton's experiments were erroneous, and asserted that the characteristic features of Khariton's apparatus caused a diffusion stream of phosphorus oxide vapour from the reaction vessel. This stream removed oxygen from the vessel, and when the McLeod gauge (which was separated from the vessel by a trap cooled with liquid air) showed a pressure p_1 the reaction vessel in fact contained no oxygen. Later he wrote that Khariton and Val'ta were trying, in their paper, to reintroduce the ideas of the existence of so-called "false" equilibria, which had been clearly shown to be erroneous early in the nineteen-hundreds by many careful studies, including his own. This paper was therefore incorrect, like all earlier papers of this sort. In conclusion, Bodenstein did not advise anyone to concern themselves with these hopeless problems.

Bodenstein's criticism appeared convincing to my colleagues at the Physicotechnical Institute, and even to my coworkers in my laboratory. Even I lived through not a few unpleasant hours. Without delay, I undertook to verify and continue Khariton's work, and with some numerical refinements confirmed his results [13-16].

I carried out a series of experiments in which the possibility of a diffusion stream was eliminated completely; in spite of this, all the unusual phenomena reported by Khariton and Val'ta were preserved.

Conclusive proof was thus obtained for one of the most surprising phenomena in nature — the sharp transition from the almost complete inertness of a substance to its vigorous reaction, with a negligible change in its density. I would remind you that in our time the existence of a similar phenomenon has made it possible to produce energy in atomic reactors and to use atomic bombs.

Let us return, however, to late 1926 and the inoffensive experiments with phosphorus. I made a thorough quantitative study of the various regular features of the phenomenon of the lower pressure limit and its dependence on the degree of dilution with inert gas, phosphorus vapour pressure, and temperature. Shal'nikov and I discovered another surprising phenomenon — the existence of critical vessel dimensions. It was found that the critical pressure is inversely proportional to the square of the diameter d of a spherical vessel. At this point we ceased to understand anything at all. It appeared that the reactivity of phosphorus is determined not only by its density but also by what seemed to be completely unrelated parameters — the volume or dimensions of the reaction vessel. We then tried to summarise all the data which we had obtained in the form of an empirical criterion for the spontaneous ignition of phosphorus vapour (analogous to that described above for thermal explosion).

This criterion had the form

$$d^2(O_2)(P_4)\left[1+\frac{(A)}{(P_4)+(O_2)}\right]=C, \qquad (5)$$

where A represents argon and the parentheses denote the partial pressures of the corresponding gases. For cylindrical vessels, the value of the constant C was found to be about 10^{-3} when the pressure is expressed in mmHg and the diameter d of the vessel is expressed in cm.

We first suggested that the oxidation of phosphorus was a Bodenstein chain reaction with alternation of the active particles (here biradicals) — O atoms and P_4O, for example, according to the scheme:

(1) $O + P_4 \rightarrow P_4O$.
(2) $P_4O + O_2 \rightarrow P_4O_2 + O$ etc. $\qquad P_4O_2 \rightarrow P_4O_{10}$.

The oxides P_4O_2 (probably also biradicals) were rapidly oxidised further to P_4O_8 and P_4O_{10} with the liberation of a large amount of energy. Even at this stage we introduced a hypothesis which departed from that of Bodenstein. We suggested that the active particles (for example O atoms), may disappear at the walls of the vessel, by adsorption (with subsequent heterogeneous reaction, for example $O + O \rightarrow O_2$). The left-hand side of the empirical expression is then found to be proportional to the length of the chain ν, that is, to the number of elementary reactions (1) and (2) between the initiation of the chain and its termination at the walls of the vessel. In 1928 Trifonov [17] in our laboratory proved by direct experiment that in the photochemical chain reaction $H_2 + Cl_2$ at a pressure of about 20 mmHg chain rupture in fact takes place almost exclusively at the walls of the vessel. The reaction rate and hence the length of the chain here was found to be proportional to d^2.

These unbranched reactions, however, take place at a constant rate $n_0\nu$, where n_0 is the number of primary P_4O radicals or O atoms initiated in one second. Their number, like the length of the chain, changes smoothly with pressure, so that this suggestion does not explain the existence of the lower limit of oxygen pressure $(O_2)_1 = P_1$.

At this point an idea occurred to us.

What if, in addition to Bodenstein's unbranched chains (Fig. 3), there also existed branched chains (occasional branching as in Fig. 4 or multiple branching as in Fig. 5)? In other words, let us assume that there is a certain mathematical expectation δ that at each step in the chain an average of one new O atom is produced by the energy of the



Fig. 3. Schematic representation of an unbranched chain reaction.

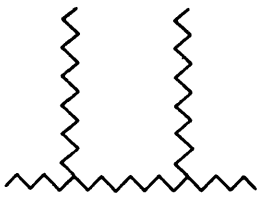


Fig. 4. Schematic represention of a chain reaction with occasional branching.

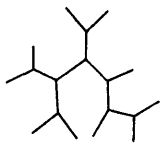


Fig. 5. Schematic representation of an intensively branched chain reaction.

oxidation of P_4O_2 to P_4O_{10}. If the branching is only occasional, δ is a small fraction. If then $\nu\delta = 1$, each act of chain termination will be compensated by the necessary production of one new chain as a result of the act of branching. When $\nu\delta > 1$ (for example, $\nu\delta = 2$), however, the number of chains will automatically increase with time, and ignition will take place. Thus the condition $\nu\delta = 1$ is the criterion for the transition from a negligible rate of reaction (with small value of n_0) to the vigorous reaction of chain ignition.

Since for each starting material the value of δ is constant, the condition $\nu = C$ is the condition for ignition; this remained to be proved.

The mechanism of the branching was still not clear. Soon afterwards, however, Leipunsky [18] passed a beam of slow electrons through phosphorus vapour burning at low pressures, and showed that the kinetic energy of the electrons increases considerably (up to 10 eV, that is, up to energies which are almost double the energy of the dissociation of oxygen into atoms). From this we concluded that in the oxidation of P_4O_2 to P_4O_{10} electronically-excited particles are produced, capable, on collision with an O_2 molecule, of bringing about the dissociation of the latter into two atoms, leading to energetic chain branching.

My paper was published in 1927. Almost immediately I received a letter from Bodenstein, in which he withdrew his objections and accepted our discovery; soon afterwards, at a meeting of electrochemists, he did this publicly. I am very grateful to Professor Bodenstein for his criticism, without which we would hardly have continued Khariton's work, and also for his subsequent systematic support of my work in this field.

A. F. Ioffe and all my colleagues in Leningrad accepted our work and congratulated us on our discovery.

In 1928 I reported the preliminary results obtained by Ryabinin [19] and myself on the chain ignition of sulphur vapour in oxygen, where the results obtained were analogous to those of the experiments on the ignition of phosphorus, and also Zagulin's results [20] on the chain ignition of $H_2 + O_2$ and $CO + O_2$ mixtures (in the last two instances the lower limit of p_1 for the mixture is observed only at a temperature above a certain critical temperature, below which no ignition takes place).

In 1928 Hinshelwood and Thompson [21] published the first results of their study of the so-called upper limit for the oxidation of mixtures of hydrogen and oxygen. Surprisingly, spontaneous ignition did not take place at pressures in the mixture greater than a certain limiting value p_2, whose magnitude decreased fairly rapidly with decrease in temperature. By combining Zagulin's data on the lower limit with Hinshelwood's data on the upper limit, it was possible to draw, on pressure–temperature coordinates, the region of spontaneous ignition in the form of a peninsula terminating in a sharp point (Fig. 6). Unlike the lower limit, the upper limit does not depend on the dimensions and state of the walls of the vessel, so long as the upper limit is not too close to the point. Hinshelwood also found that the magnitude of p_2 was influenced considerably by an inert gas, which reduced the partial pressure of the $H_2 + O_2$ mixture at the upper limit. The decrease in this partial pressure was found to be close to the partial pressure of the inert gas, so that with respect to total pressure the upper limit remained almost unchanged. The merit of Hinshelwood's work was that he interpreted the phenomenon of the upper limit within the framework of the theories of branched chain reactions. He suggested that termination at high pressures is determined by the ternary collision of the active particle with a molecule of oxygen and any other molecule M, in particular the inert gas, whereas the branching, as in the situation close to the lower limit, is determined by the binary collision of the active particle with oxygen. In this case, however, with increase in the total pressure of the mixture, the chain termination will increase in proportion to the quantity $(O_2)(M)$, whereas the branching will increase in proportion to (O_2), and at a certain total pressure p_2 the termination will become equal to the branching. At $p > p_2$, spontaneous ignition is impossible. The temperature dependence of the limiting value of p_2 is related to the activation energy of the branching process, since chain termination, which takes place on ternary collisions, involves almost no activation energy.

The chemical mechanism of the oxidation of hydrogen became known only after Lewis [22] put forward his celebrated scheme for this reaction. It was found that the branching is associated with the reaction of an H atom with oxygen: $H + O_2 \rightarrow OH + O$ followed by the rapid reaction $O + H_2 \rightarrow \rightarrow OH + H$, whereas termination in the bulk is associated with the reaction $H + O_2 + M \rightarrow HO_2 + M$. Under these conditions HO_2 is a radical with low activity, incapable of propagating the chain. For many reactions taking place at relatively low temperatures, where an important part is played by the presence of oxygen atoms, chain termination by the reaction $O + O_2 + M \rightarrow O_3 + M$ is possible, as shown by Hinshelwood and Dalton [23].

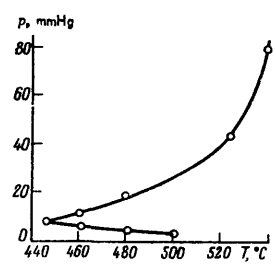


Fig. 6. Range of ignition of hydrogen [20].

Since chain termination may take place both at the walls of the vessel and within the vessel (by ternary collisions), I put forward in the early nineteen-thirties a quantitative theory of the entire field of spontaneous reactions.

In 1929 my coworkers and I showed that an analogous ignition peninsula is observed for the reaction $CO + O_2$.[20] Similar regions of chain spontaneous reaction are characteristic of many other oxidations, for example, the oxidation of phosphine[24] (Fig. 7) and silane[25] (Fig. 8).

Early in 1928, I published papers[3,4] on the two types of spontaneous reaction. The theory of thermal spontaneous reaction outlined above was described for the first time, and the first ideas were put forward regarding chain spontaneous reaction and the development of the chain avalanche.

I propose to describe here the theory of branched chain reactions in the form in which we put it forward several years later[26-29].

It can readily be seen that when one type of active particle (atoms or radicals) is present, the kinetic equation determining their concentration n is of the form

$$\frac{dn}{dt} = n_0 + (f-g)n, \qquad (6)$$

where fn is the rate of the branching reaction, gn the rate of chain termination, and n_0 the number of active centres produced in one second as a result of thermal motion. At constant concentrations of the original gases or at the start of the reaction, when combustion can be neglected, f and g are constant quantities. At low pressures, when the disappearance of the active centres is determined by their capture by the walls of the vessel, the value of g (for a probability ϵ of capture by the wall equal to 1) for cylindrical vessels is given by the equation

$$g = \frac{25.2D_0}{d^2p},$$

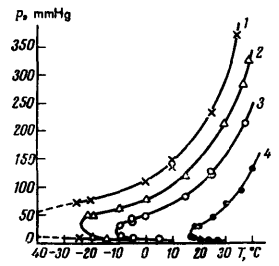


Fig. 7. Range of ignition of phosphine[24]: 1) 57% PH_3; 2) 43% PH_3; 3) 22% PH_3; 4) 10% PH_3.

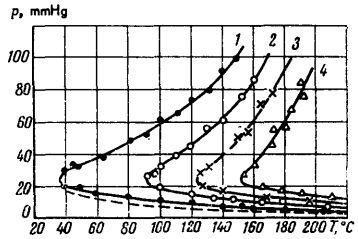


Fig. 8. Range of ignition of silane[25]: 1) 49% SiH_4; 2) 39% SiH_4; 3) 30% SiH_4; 4) 14% SiH_4.

where D_0 is the diffusion coefficient of the active centres at p = 1 mmHg, and d the diameter of the vessel. At very low values of ϵ we have $g = \epsilon u/d$, where u is the thermal velocity of the active particles. The values of g for intermediate values can be found from papers published by Lewis and myself. By treating the walls of a glass or quartz reaction vessel with various substances or in other ways, it is possible to vary the value of the limit p_1 over a wide range (by a factor of up to 100) for a given diameter.

As a rule, in all chain reactions we are dealing with not one but several (a minimum of two) active centres (for example P_4O and O), and hence we are dealing with not one but two or several kinetic differential equations. Usually, however, one of these active particles reacts much more slowly than the other, and this makes it possible, with a certain degree of approximation, to reduce the system of differential equations to one differential equation, which describes the change in the concentration of this least active centre, whose concentration is much greater than that of the others. Then, of course, the constant f becomes a complex quantity including the reaction rate constants of all the centres. By integrating Eqn. (6), we obtain:

$$n = \frac{n_0}{f-g}(e^{(f-g)t} - 1) = \frac{n_0}{\varphi}(e^{\varphi t} - 1) \quad \text{for } (f-g) = \varphi > 0, \qquad (7)$$

$$n = n_0 t \quad \text{for } (f-g) = \varphi\, 0, \qquad (8)$$

$$n = \frac{n_0}{g-f}(1 - e^{-(g-f)t}) \quad \text{for } (f-g) = \varphi < 0. \qquad (9)$$

The equality $f = g$ is simply the criterion determining the limit. For $f > g$, the concentration of active centres increases exponentially with time. The reaction rate $w_t = kn$ (where $1/k$ is the mean time required for the active centre to react with the original molecule) increases according to the same exponential law. The quantity of substance x which has reacted at moment of time t also increases exponentially with time: $x_t = \int_0^t w_t dt$. For infrequent chain branching we have $k \gg f$, and for intensive chain branching we have $k = f$. Subsequently, we shall consider the development of chain branching at pressures which are only slightly greater than the lower limit, since at these pressures, as a result of the high thermal conductivity, the increase in the temperature of the mixture during the reaction is small.

Close to the lower limit, $\frac{g}{f} = \frac{p_1}{p_0}$, where p_1 is the pressure of the lower limit, and p_0 the original pressure of the mixture above the lower limit.

It follows from formula (7) that the reason for the chain avalanche is the rapid increase in the number of active centres capable of reacting. Even at low pressures, exceeding the lower limit by a factor of only 1.5–2, the value of f is very large and varies from several tens to several hundred reciprocal seconds. Thus the development of the reaction with time takes place within tenths or even hundredths of a second.

For $f < g$ the reaction rate is always less than the quantity $n_0 t$ and soon reaches a steady value (in the absence of appreciable combustion) $w = kn = \frac{kn_0}{g-f}$ or (for intensive chain branching, when $k \simeq f$):

$$w = \frac{n_0}{(g/f-1)} = \frac{n_0}{p_1/p_0 - 1}, \qquad (10)$$

where $p_0 < p_1$ (for $f < g$).

Thus the characteristic feature for branched reactions taking place under the limit is a rapid increase in rate, which does not correspond to the increase for ordinary reactions, as the limit is approached (Fig. 9). For $p_1/p_0 = 1$, the rate naturally does not tend towards infinity, but reaches values kn_0t, that is, it begins to increase linearly with time. The closer we are to the limit, the greater the time required for the steady rate to be reached. Even for $\frac{g}{f} - 1 = 0.01$, however, that is, when the value of p_0 is only 1% less than p_1, the reaction rate will in practice reach a steady state within one second.

In order to show clearly the change in the reaction rate w and the quantity x of substance reacted as a function of time, we can construct, for intensive chain branching with $n_0 = 10^3$, $f = 500$, and different values of the ratio p_1/p_0, corresponding curves for the quantity x, on a smaller scale for $f > g$ and on a much larger scale for $f < g$ (Figs. 10 and 11).

It should be noted that the quantity n_0, that is, the rate of spontaneous initiation of the primary radicals, is relatively very small. In actual fact, this process is associated with the production of the primary active particles — free atoms and radicals — from neutral molecules under the influence of thermal motion. Almost no thermal dissociation of the original molecules to give two free atoms or radicals takes place at room temperatures. The production of free radicals as a result of reaction between the original molecules, for example, $P_4 + O_2 \rightarrow P_4O + O$ or $H_2 + O_2 = 2OH$, has a much higher probability. Even these processes, however, are associated with a fairly large activation energy, so that n_0 is always small. It should, however, be noted, that the growth of the chain avalanche takes place so rapidly that the appearance of only a few primary active particles is sufficient to lead to their production in vast quantities within one second.

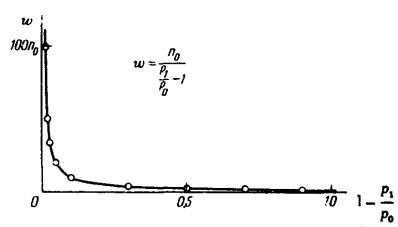


Fig. 9. Dependence of w on p_1/p_0 (for $f < g$).

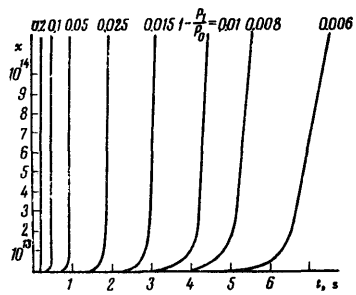


Fig. 10. Dependence of x (quantity of substance reacted) on t at various values of p_1/p_0 (n_0 = $= 10^3$ mole cm^{-3} s^{-1}; for $f > g$; $f = 500$ s^{-1}).

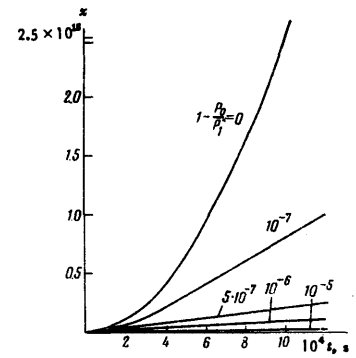


Fig. 11. Dependence of x on t at various values of p_1/p_0 ($n_0 = 10^3$ mole cm^{-3} s^{-1}; $f < g$).

It is possible in principle, however, to have instances where even one active centre is produced very rarely. We encountered such a case in a study, with Ryabinin [19], of the ignition of sulphur. Above the lower limit here ignition took place only rarely, and usually no ignition was observed. When a weak discharge was passed through the cylinder containing the oxygen, however, and the oxygen was then passed into the vessel containing the sulphur, ignition was always observed above the lower limit.

We would remind you that in atomic bombs a neutron source is used for the same purpose.

Since the value of n_0 is always very small (at a pressure $p \leqslant p_1$), the reaction rate is equal to almost zero and conditions for the development of a chain avalanche are not created. At a pressure only slightly greater than p_1 the reaction rate increases rapidly to extremely high values within a fraction of a second.

The first experimental verification of the theory of branched chain ignition was obtained in our Institute by Koval'skii [30] for the example of the oxidation of detonating gas ($2H_2 + O_2$) at 485° and various p_1/p_0 ratios (Fig. 12). From this it was possible to determine the value of f and hence the branching constant [31]. The exponential growth of the avalanche is confirmed up to a degree of conversion of 20–30% (Fig. 12). The curves for high degrees of conversion are distorted because of the decrease in the concentration of the original gases. A complete analysis of

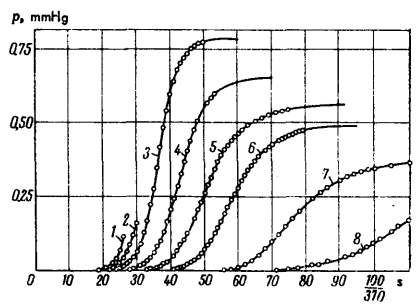


Fig. 12. Kinetics of the oxidation of a $2H_2 + O_2$ mixture at 485° and various initial pressures (mmHg): 1) 8.2; 2) 7.8; 3) 7.4; 4) 7.1; 5) 6.8; 6) 6.4; 7) 6.1; 8) 5.8. [30]

the curves for the development of the chain avalanche was made difficult by the lack of reliable data on the chemical mechanism of the reaction. The experimental verification of the theory became much easier after Lewis[22] put forward his scheme for the oxidation of hydrogen.

When applied to a pressure near the lower limit, this scheme for the oxidation of hydrogen, for which rigorous experimental verification was subsequently obtained, can be written in the form:

(1) $OH+H_2 \rightarrow H_2O+H$,
(2) $H+O_2 \rightarrow OH+O \rightarrow$ chain branching,
(3) $O+H_2 \rightarrow OH+H$,
H+ wall, O+ wall, OH+ wall $\rightarrow$ chain termination.

It is assumed that the chains are initiated by the reaction $H_2 + O_2 \rightarrow 2OH$. The smallest reaction rate (particularly when the mixture contains an excess of hydrogen) is that of the reaction $H + O_2 \rightarrow OH + O - 17$ kcal. This is the only endothermic step. From this it was concluded that in mixtures with an excess of hydrogen over the stoichiometric quantity, the highest concentration in the course of the reaction will be attained by H atoms. By using the method of quasi-steady concentrations for the change in the concentration of H with time, we obtain the expression:

$$\frac{d[H]}{dt} = n_0 + (2a_2 - a_2')[H] = n_0 + 2a_2\left(1 - \frac{a_2'}{2a_2}\right)[H], \qquad (11)$$

where $f = 2a_2 = 2k_2[O_2]$; $g = a_2'$; $n = [H]$; and $(1 - a_2'/2a_2) = (1 - p_1/p_0)$.

We can also write a differential equation for the rate of consumption of oxygen:

$$\frac{d[O_2]}{dt} = n_0 + k_2[O_2][H]. \qquad (12)$$

By solving the system of differential equations (11)–(12), we can calculate the entire course of the reaction from its initiation to complete combustion. I published this work in 1944.[32] Nalbandyan and Karmilova[33] in 1958 repeated Koval'skii's experiments[30] on the study of the value of Δp as a function of t, much more extensively and in much more detail. From these experiments it was possible to determine the constant k_2 for the branching reaction, and then to compare with experiment all the theoretical relationships which I had obtained. The agreement was found to be exceptionally good. Here it was also shown that the ratio $f/g = 2a_2/a_2'$ is in fact equal to p_0/p_1. It was also shown[32] that in the reaction $2H_2 + O_2$ at $p_1/p_0 = 0.5$, the concentration (or partial pressure) of H atoms at 50% consumption of the original oxygen should amount to 30% of that of the original oxygen and hence to 60% of the reacted oxygen, or 30% of the partial pressure of the water formed. Correspondingly, at $p_1/p_0 = 0.25$ the pressure of H atoms at the maximum will amount to 80% of that for the original oxygen, and at $p_1/p_0 = 0.7$ to about 10% of that of the original oxygen (Fig. 13). All these relationships are observed at a temperature of about 500°, when there is almost no equilibrium dissociation of water. This quite surprising result could essentially have been obtained from our theory ten years earlier.

When chain termination is neglected, the result of Lewis' three elementary reactions can be expressed by the following stoichiometric relationship: $H + 3H_2 + O_2 = 3H + 2H_2O +$ + 13 kcal or $3H_2 + O_2 \rightarrow 2H_2O + 2H$. We see that the chemical energy liberated in the formation of water according to

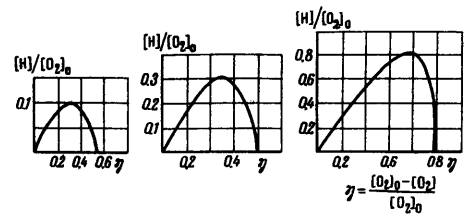


Fig. 13. Dependence of [H] on $\eta = \frac{[O_2]_0 - [O_2]}{[O_2]_0}$ at various values of p_1/p_0.[32]

the reaction $2H_2 + O_2$ is used up in the dissociation of H_2, thus maintaining the rapid development of the chain avalanche. At the end of the reaction, all the H atoms naturally recombine on the wall of the vessel, forming H_2 or H_2O molecules. This is accompanied by the liberation of an additional quantity of energy. A process taking place with the build-up of an atomic H concentration equal to twice the concentration of the original oxygen could in principle be carried out in vessels with a large radius (for example 10 m) with walls treated in such a way that the value of ϵ was very small. Here the pressure p_1 would be negligibly small, of the order of several ten-thousandths of a millimetre, and by carrying out the experiment at a pressure of say 0.1 mmHg, chain termination at the walls and within the vessel by ternary collisions $H + H + M \rightarrow$ $\rightarrow H_2 + M$ could be neglected. Then the rate at which the rapidly-formed atomic hydrogen disappeared as a result of chain termination in the interior of the vessel and at the walls would be so slow that at the end of the reaction we would have in the vessel as many H atoms as water molecules. This would make it possible to use this method of preparing atomic hydrogen for all sorts of reductions, for example, the reduction of oxides. The practical utilisation of this reaction is hindered by the fact that the pressures in the system are too low. An increase in the pressure to 10 mmHg, which would increase the quantity of atomic hydrogen by a factor of 100, would require such rapid rates of flow that the atomic hydrogen could not be prevented from recombining by ternary collisions.

This surprising conclusion regarding the vast relative concentrations of atomic hydrogen was confirmed experimentally by Kondrat'eva and Kondrat'ev[34]. They determined the concentration of free atoms from the increase in temperature recorded by a thermocouple placed in detonating gas burning at a pressure slightly greater than p_1, and confirmed the theoretical conclusion that the concentration of atomic hydrogen reaches 20–30% of the original concentration of oxygen in the mixture. Kondrat'ev's method, however, was nevertheless not quite a direct method of chemical analysis. The theory was subsequently confirmed thanks to an idea of Voevodskii's. In ordinary chain reactions the concentrations of atoms and radicals are too low to permit their detection by the EPR method. In branched chain reactions, however, where these concentrations are incomparably greater, the EPR method can be used successfully, as proved experimentally by Voevodskii and coworkers[35]. The method made it possible to determine not only the quantity of free radicals, but also their chemical composition. In 1960 Voevodskii showed that the concentration of atomic hydrogen does in fact reach the values indicated above.

Subsequently, Kondrat'ev and Nalbandyan[36], using the same method, detected considerable quantities of atomic oxygen in the $H_2 + O_2$ flame; the concentrations were found to be greatest in mixtures poor in hydrogen. Soon afterwards, the same authors[37] were able to record the EPR signals of OH radicals in the hydrogen flame and to determine their concentrations at various compositions of the mixture (Fig. 14). In the stoichiometric mixture the values of [H] reach 10^{16} molecules cm^{-3}, that is, about 1 mmHg. Earlier, it had been assumed (on the basis of the values for the rate constant of the reaction $O + H_2 \rightarrow OH + H$, given by Harteck and Kopsch[38]), that the concentration of O atoms was much smaller, by about 2 orders of magnitude, than that corresponding to the above observations. The value for the rate constant of the reaction $O + H_2 \rightarrow OH + H$, recently determined by Azatyan[39,40] by the method of limits, shows good agreement with the observed concentrations of atomic oxygen. The values of the concentration of OH radicals measured by the EPR method also agree with the value of the rate constant for the reaction $OH + H_2 \rightarrow H_2O +$ + H, determined by Avramenko[41] and Kondrat'ev[42].

The EPR method was also applied to the oxidation of carbon monoxide. Nalbandyan and coworkers[43-47] made a detailed study of rarefied carbon monoxide flames with oxygen in the presence of small quantities of substances acting as hydrogen donors. (Absolutely dry mixtures of CO and O_2 containing no hydrogen donors are incapable of spontaneous ignition.) H_2 and other donors were used as additives. In complete accordance with the chain branching mechanism, the combustion of CO in the presence of H_2 can be represented by the following scheme:

$$H_2+O_2\rightarrow 2OH \quad \text{(chain initiation)},$$
$$OH+CO\rightarrow CO_2+H,$$
$$H+O_2\rightarrow OH+O,$$
$$O+H_2\rightarrow OH+H,$$
$$\left.\begin{matrix} H+\text{wall} \\ O+\text{wall} \\ OH+\text{wall} \end{matrix}\right\} \rightarrow \text{chain termination}.$$

In a rarefied flame of this mixture in the presence of small quantities of added H_2, Nalbandyan and coworkers were able to detect high concentrations of atomic oxygen, hydrogen, and OH radicals, whose concentrations were found to be in good agreement with the OH concentrations previously measured by Kondrat'ev[41,42,48-50] from the electronic absorption spectra. Thus all the types of active centre assumed to be responsible for chain branching in this system were identified.

When small quantities of H_2 were added, O atoms predominated in the flame, and when large quantities of H_2 were added, H atoms predominated in the flame (see Fig. 15, which gives the concentrations of H, O, and OH for the same $CO + O_2$ mixture containing different quantities of added H_2). The concentrations of H and O atoms were always much greater than the concentration of OH radicals[51]. In the Institute of Chemical Physics of the Academy of Sciences of the USSR, Azatyan and coworkers[39,40] put forward a method for determining the rate constants for the reaction of atomic oxygen and hydrogen with the molecules of various substances, making use of the decrease in the lower limit of spontaneous ignition for the combustion of a mixture of CO and O_2 in the presence of small quantities of added H_2 or other hydrogen donors.

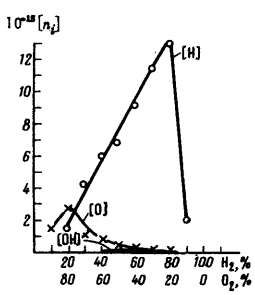


Fig. 14. Dependence of the concentrations of H, O, and OH on the initial composition of the hydrogen–oxygen mixture[37].

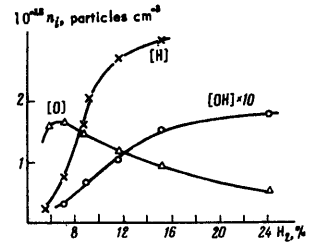


Fig. 15. Dependence of the concentrations of H, O, and OH on the initial concentration of H_2 in the CO flame[51].

This method was used to determine the values of the rate constants for all the fundamental elementary reactions in rarefied flames of hydrogen and carbon monoxide. Using these constants, it was possible to calculate by means of an electronic computer the time dependence of the concentrations of H_2O and OH during the reaction and to compare the results with the experimentally observed (by the EPR method) changes in the concentrations of all the active particles with change in the flow velocity[52]. The flow velocity can be regarded as a quantity corresponding to the reaction time. Fig. 16 gives the calculated (on the left) and experimental (on the right) values of the change in the concentrations of O, H, and OH in the flame for a $CO + O_2 + 6\%$ H_2 mixture, and shows that the curves are of similar shape. The discrepancy of 20% in the absolute values of the concentrations ought to be attributed primarily to the difference in the conditions of reaction in a flow system (in which the experiments were carried out) and the static system assumed for the calculations. The discrepancy is evidently related chiefly to the fact that no allowance was made for the diffusion of atoms in the flow system.

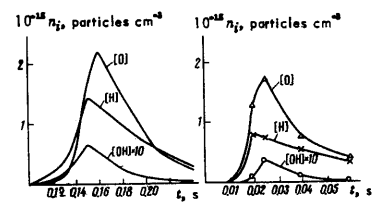


Fig. 16. Comparison of the time dependences of the concentrations of O and H atoms and OH radicals in the $2CO + O_2 + 6\%$ H_2 flame, obtained by calculation (on the left) and by experiment (on the right).[52]

TABLE. $H_2 + O_2$ mixture. p = = 2.96 mmHg, T = 993°K.

	H	O	OH
$10^{-16}(n_i)_{exp}$	6	0.8	0.16
$10^{-16}(n_i)_{theor}$	6.2	0.81	0.15

The calculated and experimental values of the H, O, and OH concentrations for an $H_2 + O_2$ mixture are given in the Table [53] (for the same interval). Such good agreement is probably accidental.

It is important to apply the EPR method to the study of the mechanism of other branched reactions, such as the combustion of phosphorus, sulphur, carbon disulphide, etc. Work in this direction has only begun to develop in our Institute.

I now wish to turn to work, carried out recently in our Institute, which has extended considerably our ideas on branched chain reactions and has shown that the number of reactions with a branched-chain mechanism is much greater than was previously supposed.

As already shown, branching is always associated with utilisation of the energy of the chemical reaction. At an early stage in the development of the chain theory [16,26], I imagined that branching takes place as a result of the formation, in the course of the reaction, of energetically excited particles, with an excess of vibrational or electronic energy, which could give up the excitation energy to molecules of the starting materials, leading to their dissociation into atoms and radicals.

Although these ideas gave a consistent and extremely general explanation for the course of branched chain reactions, the idea that excited particles take part in the branching was in fact left aside and until recently was almost never discussed in the literature.

In fact, according to modern physical theories, the simultaneous transfer of several quanta of vibrational energy when particles collide is extremely improbable.

Although the transfer of energy from electronically--excited molecules is possible, the probability of formation of electronically-excited particles in chemical reactions is generally very low.

Moreover, as we saw for the example of the oxidation of hydrogen, branching in this reaction takes place without excited particles, by the reaction $H + O_2 \rightarrow OH + O$ followed by $O + H_2 \rightarrow OH + H$. Thus it would seem that branching involving excited particles is impossible or unlikely. Nevertheless, in order to explain many phenomena observed in chain reactions, particularly in fluorination, it has in recent years become necessary to return again to the idea that a part in branching is played by energetically-excited particles, products of the exothermic elementary reactions of chain propagation.

An important addition to the old ideas, however, is the observation that the branching takes place not by the transfer of energy from an excited product molecule to a molecule of the original reagent, but by chemical reaction of the excited product molecule with the formation of atoms and radicals.

This chemical reaction may be either unimolecular decomposition of the excited molecule or its bimolecular reaction with a molecule of the original reagent.

I shall explain this with reference to several examples of fluorination, studied in Shilov's laboratory [54] in our Institute.

One of the stages in chain fluorination is the reaction

$$R + F_2 \rightarrow RF + F.$$

This reaction is so exothermic that the heat of the reaction sometimes exceeds the energy of the weakest bond in the RF^* molecule being formed. This molecule may therefore undergo unimolecular decomposition with the formation of atoms and radicals, leading to chain branching. For example, in the reaction of fluorine with methyl iodide, the chain is propagated according to the reactions

$$\text{(a)}\ F + CH_3I \rightarrow HF + CH_2I,$$
$$\text{(b)}\ CH_2I + F_2 \rightarrow CH_2FI^* + F.$$

The energy of the C–I bond in the CH_2FI^* molecule is less than the heat of reaction (b). The CH_2FI^* molecule may therefore dissociate immediately after its formation:

$$CH_2FI^* \rightarrow CH_2F + I$$

and the CH_2F radical reacts further with F_2:

$$CH_2F + F_2 \rightarrow CH_2F_2 + F.$$

When fluorine is mixed with methyl iodide, flames are produced immediately, even at very low pressures of the reagents. The probability of branching is apparently so high that the range of spontaneous reaction extends over all pressures attainable in practice.

The most important proof of this mechanism was provided by the discovery of high concentrations of I atoms in the reaction zone by the EPR method. It was shown that the concentration of I atoms reaches more than 10% of the concentration of original F_2. [55] At the same time there is almost no increase in temperature in the reaction zone (the reaction is carried out at very low pressures).

An interesting feature is that whereas in the gaseous phase the reaction of CH_3I with F_2 takes place very readily, and iodine is liberated in accordance with the proposed mechanism, fluorine does not liberate iodine from methyl iodide in solution in an inert oil. This means that in the reaction there is still in principle an upper limit, produced by loss of energy from the excited CH_2FI^* molecules on collision with surrounding molecules [56].

The kinetics of the reaction of fluorine with methyl iodide were recently calculated theoretically on an electronic computer on the basis of elementary stages including the proposed branching reaction. The data obtained for the composition of the products at different reagent ratios showed good agreement with experiment.

Another type of branching reaction is observed in the addition of fluorine to alkenes. For example, in the fluorination of tetrafluoroethylene, the C_2F_5 radical produced by the addition of an F atom to the alkene may undergo unimolecular decomposition with rupture of the C–C bond according to the reactions

$$F + C_2F_4 \rightarrow C_2F_5^* \rightarrow CF_3 + CF_2.$$

In actual fact, the overall heat of these two reactions is positive and amounts to ~ 20 kcal mole^{-1}, that is, the heat of the first reaction is sufficiently great to ensure subsequent dissociation of the radical. This leads to branching,

since the reaction of CF_2 with F_2 leads to the formation of two new F atoms:

$$CF_2+F_2\rightarrow CF_3+F,$$

$$CF_3+F_2\rightarrow CF_4+F.$$

A flame is readily produced when fluorine is mixed with tetrafluoroethylene. In accordance with the mechanism of a chain-branched reaction, very large concentrations of F atoms were detected in the reaction zone during the fluorination of C_2F_4.

If the excitation energy of the radical formed by the addition of the F atom to the alkene is insufficient to bring about its decomposition, branching may take place as a result of its subsequent reaction with F_2. The two successive reactions lead to the accumulation of sufficient energy for unimolecular decomposition of the resulting molecule, leading to branching.

Study of the gas-phase reactions of fluorine with tetrachloroethylene and dibromoethylene by the EPR method showed that very high concentrations of F and Cl atoms are formed in the reaction zone for the first compound, and very high concentrations of F and Br atoms in the second, confirming the suggestion that these reactions are branched chain reactions.

When the excitation energy is insufficient for unimolecular dissociation of the bond, branching may take place by the bimolecular reaction of an excited molecule of the reaction product with a fluorine molecule. The mechanism of formation of the radicals in the bimolecular reaction of valency-saturated molecules is less usual than unimolecular decomposition of a molecule, so that I would like to remind you of it at this stage.

In 1954, I suggested[29] that the activation energy of the endothermic reaction $RX + IR \rightarrow R + XI + R - q$ is close to the endothermicity q, and that its activation barrier is close to zero.

In reality, examination of the reverse reaction, in which two R radicals attack the XI molecule, indicates that its activation barrier is probably even smaller than that for the reaction $R + XI \rightarrow RX + I$, and we know that the activation barrier for reactions of radicals with molecules usually does not exceed a few kilocalories per mole. From the principle of detailed balance, it follows that the reaction of two molecules with the formation of two radicals will also have a low activation barrier.

These ideas were confirmed theoretically for the simplest reaction of two hydrogen molecules:

$$H_2+H_2\rightarrow H+H_2+H.$$

In addition, special experiments were carried out in our Institute to record radicals directly by the EPR method for those instances where the consumption of energy in the reaction is small.

Molecular fluorine is an example of a molecule for which bimolecular reactions of the type $F_2 + HR \rightarrow F + HF + R$ are particularly favourable, since they do not involve the consumption of a large amount of heat and may even be exothermic. Most chain fluorination reactions are initiated thus[57].

The activation energy of these reactions is apparently always less than the excitation energy of the molecules formed in the exothermic reactions of chain fluorination. Thus the same bimolecular reaction involving the formation of radicals from two molecules may also take place in the branching. The excited molecules of the product may react with F_2 without any additional activation energy, and this makes chain branching possible.

The simplest example is the fluorination of hydrogen. In this case, in the chain analogous to the Nernst chain for the reaction of hydrogen with chlorine: $F + H_2 \rightarrow HF + H$; $H + F_2 \rightarrow HF + F + 98$ kcal; the second reaction is exothermic to the extent of 98 kcal; this is more than twice the energy of the F–F bond.

The reaction

$$F_2+HF\rightarrow F.\,\boxed{.F\ldots H.}\,.F\rightarrow F+HF+F-38\ \text{kcal}, \qquad (I)$$

requires the consumption of 38 kcal, corresponding to the dissociation energy of fluorine. It may be assumed that the greater part of the HF* molecules formed in the elementary act $H + F_2 \rightarrow HF + F + 98$ kcal will carry the greater part of the energy of this reaction, for example, 60 kcal. This is much greater than the energy consumption and corresponds to the activation energy of process (I).

Thus here branching takes place by the reaction of an excited HF* molecule with F_2. The results of experiments confirm this suggestion. It was found that the range of spontaneous reaction between hydrogen and fluorine is bounded by clearly defined upper and lower pressure limits, and this is one of the characteristics of a branched chain reaction[58].

It should be noted that the reaction of fluorine with hydrogen has always appeared puzzling, and different authors have obtained extremely contradictory results.

Thus Eyring and Kassel[59] stated that although a mixture of hydrogen and fluorine explodes readily, they were able to prepare mixtures which were stable at room temperature and a total pressure of the reagents equal to atmospheric pressure.

Others (Grosse and Kirschenbaum[60]) attributed these results to experimental errors and showed that a mixture of hydrogen and fluorine always ignites at room temperature.

Consideration of the mechanism of chain ignition indicates that these contradictions are apparently due to the fact that the first authors worked with mixtures inside the ignition peninsula whereas the others worked outside this peninsula. It should also be noted that chain termination within the interior of the vessel takes place by reaction with oxygen, so that the position of the upper limit depends to a marked extent on the concentration of oxygen impurity in the fluorine.

In all these examples it can be seen that the excited molecules of the product do not transfer energy to the original molecules. At the same time it is this energy which is used directly in the chemical reactions leading to the formation of atoms and radicals which begin new chains, so that it brings about branching in this way. Thus the old ideas of the important part played by excited molecules in branching find application here. In this connection it may be noted that in any exothermic reaction of an atom or radical with a molecule, the molecule of the reaction product initially has considerable vibrational excitation energy. A number of instances have been recorded where the greater part of the energy of the reaction is concentrated in vibrational degrees of freedom of the molecule.

Data on the dissipation of vibrational energy show that this process takes place fairly slowly according to the same principle (of which mention was made earlier) — the low

probability of multi-quantum transitions — and, which is most important, for large vibrational quanta the transfer of even one quantum usually requires 10^3–10^4 collisions.

Even in the light of the above discussion, however, we would not expect that the probability of branching would be close to unity, that is, that the chain branching would be intensive. For a chain avalanche to develop, however, it is sufficient that there be more than one branching in the total length of the chain, that is, that the probability of branching be greater than $1/\nu$. Since the lengths of the main chains in such reactions are very great, at least from hundreds to tens of thousands, this order of probability of branching is sufficient to ensure a mechanism of developing chain avalanche.

The probability of branching is determined to a considerable extent by the energy liberated in the elementary reactions of chain branching. It is therefore not surprising that so many branched chain processes have been discovered in gas-phase reactions of molecular fluorine, for which the elementary reactions are particularly exothermic. We may justifiably say that chain gas-phase fluorination is almost entirely associated with the range of branched chain reactions.

Other branched-chain reactions which have been well studied are those involved in gas-phase oxidation by molecular oxygen. Here also, branching is brought about by chemical energy, as a result of the formation of stable H–O and C–O bonds, the O–O bond being comparatively weak. The elementary processes here are less exothermic than in fluorination, so that in the gaseous phase we have both branched reactions and unbranched (or degenerately-branched) chain reactions.

Branched chain reactions are not restricted to oxidation and fluorination, however. It is known, for example, that the decomposition of NCl_3 to N_2 and Cl_2 is a branched-chain process exhibiting an upper limit[61]. The energy for branching here is undoubtedly provided by the very high bond energy in the N_2 molecule formed (225 kcal mole^{-1}). In this connection, other reactions involving decomposition with the liberation of N_2 ought to be studied. It is possible that the example of NCl_3 is not an exception.

There are other examples of chain reactions where the chain-branching hypothesis explains the observed relationships. Thus clearly defined limiting phenomena are observed in the chlorination of acetylene, according to data obtained by Shtern (in this country) and Porter (in England). It should be noted that a particularly large amount of energy is liberated in the chlorination of acetylene compared with the chlorination of other compounds.

Finally, flashes of cold flame are observed at certain pressures and temperatures in the gas-phase nitration of alkanes, as shown by Shtern[62]. Here also, a unique part is played by the formation, in the course of the elementary exothermic act, of a product which contains an excess of energy and is therefore able to undergo unimolecular decomposition with the formation of radicals.

Thus the liberation of various forms of energy in chain reactions is used to accelerate these reactions, creating the conditions for an explosion. The energy concentrated in individual molecules in the form of vibrational or electronic excitation is used for branching in chain spontaneous ignition.

This principle of the utilisation of the energy of a chain reaction can be examined on a much wider basis and applied to molecules possessing considerable chemical energy. The intermediate formation of molecules, such as peroxides and aldehydes, which are not excited but possess a considerable reserve of chemical energy relative to the final reaction products (for example, CO_2 and H_2O), may give slow branching, as a result of their kinetic instability, a phenomenon which I have named "degenerate branching".

A very large number of gas-phase and liquid-phase oxidations are known to take place by a mechanism involving these degenerately-branched chain reactions.

In conclusion, I would like to report some results on unbranched polymerisation reactions at low temperatures.

In 1960–1961 Enikolopyan, Gol'danskii, and coworkers[63] in the Institute of Chemical Physics of the Academy of Sciences of the USSR, and later other workers[64,65], in other institutes in this country and abroad, showed that in the solid-phase polymerisation of a number of monomers (acrylonitrile, vinyl acetate, methyl methacrylate, formaldehyde, etc.) under the influence of electrons with an energy of 1.5 MeV, the reaction rate is independent of temperature over a wide range of irradiation temperatures (reaching 77°K). The dependence of the initial rate of polymerisation of acrylonitrile on the reciprocal of the temperature is shown in Fig. 17. It can be seen that the rate of polymerisation in the liquid phase decreases with decrease in temperature in accordance with a value for the activation energy E = 3000 cal mole^{-1}, but at the freezing point (m.p. = 355°K) the rate increases by a factor of 25 and subsequently remains unchanged down to 77°K. In other words, the effective activation energy in the solid phase is zero. Generally speaking, on going from the liquid to the solid phase, the rate may increase considerably (acrylonitrile and formaldehyde), decrease considerably (methyl methacrylate), or remain almost unchanged (vinyl acetate)[63]. The striking feature always, however, is that the rate is constant over a wide temperature range in the solid phase, from 77°K to the melting point.

It is now known that many other monomers polymerise in the solid phase with zero activation energy.

Other forms of polymerisation temperature dependence are also known. For example, almost no polymerisation of hexamethylcyclotrisiloxane (HMCTS) takes place in the liquid phase, but the rate of the process increases sharply as the freezing point is approached, reaches a maximum in the solid phase close to this point, and with further decrease in temperature the rate again decreases and gradually reaches a plateau which extends down to 77°K (Fig. 18).

In the polymerisation of phenylacetylene there is no sharp change in activation energy on passing through the melting point (Fig. 19)[63], and with decrease in temperature the reaction rate continues to decrease slowly, showing only a slight tendency to form a plateau close to 77°K.

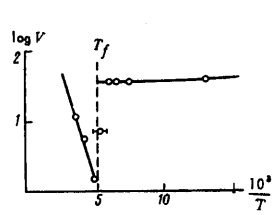


Fig. 17. Temperature dependence of the rate of polymerisation of acrylonitrile[63].

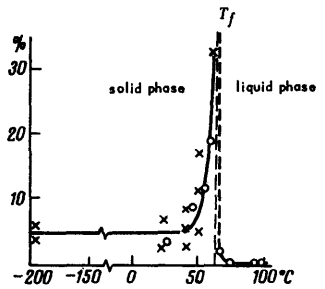


Fig. 18. Temperature dependence of the rate of polymerisation of hexamethylcyclotrisiloxane [63].

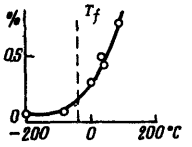


Fig. 19. Temperature dependence of the rate of polymerisation of phenylacetylene [63].

There remained doubts, however, as to whether the polymerisation takes place during the irradiation of the specimen or only during its subsequent treatment (de-freezing and isolation of the polymer). To investigate this problem, Barkalov and coworkers [66] used a special calorimeter to record the thermographic thawing curves as vinyl acetate, which had previously been irradiated at -196°C, was gradually heated. Two heat-liberation peaks were detected, close to the temperature of the phase transformation of vinyl acetate at -129°C and close to the melting point at -93°C. The same experiment was carried out without any irradiation. The thermographic curves obtained in the two experiments practically coincided, showing that no polymerisation takes place under the conditions of thawing. If polymerisation had taken place during thawing, the curves from the two experiments should have been different, because of the additional liberation of the heat of polymerisation in the first experiment.

Barkalov and coworkers [67], using a specially constructed differential thermocouple, made direct measurements of the heat liberated during the irradiation of acrylonitrile at -196°C, and hence the rate of polymerisation and the total quantity of heat liberated. It was found that the rate of polymerisation and the total quantity of heat are very close to those from the kinetic curves measured from the yield of polymer after thawing. This proved that the entire polymerisation took place at low temperature directly under the influence of the beam. Unfortunately, it was possible to carry out only a few of these experiments because of the destruction of the calorimeter.

In France, Bensasson and Dworkin [68], in Magat's laboratory, repeated the experiments with acrylonitrile and recorded the thermographic thawing curve. On the basis of these experiments they concluded that ~30% of the polymerisation takes place at -196°C during the irradiation and that the remaining ~70% takes place close to the phase transformation of acrylonitrile in the range from -140° to -100°C during the thawing.

Recently, Tal'roze and Kritskaya [69], in the Institute of Chemical Physics, carried out experiments on the polymerisation of acrylonitrile under slightly different conditions (a thin film of the frozen monomer was irradiated with electrons with an energy of 2 keV, whose path in the substance was much less than the thickness of the film and amounted to only 0.25 μm), using an extremely efficient adiabatic calorimeter. The measurement of the heat liberation was carried out directly under the beam. The experiments which they carried out in 1964 showed that rapid polymerisation takes place at the temperature of the phase transformation (-135°C) whereas, according to the latest data from the experiments which they continued, no reaction takes place at -196°C.

Thus the three groups of authors obtained contradictory results in the study of the polymerisation of acrylonitrile: the first group concluded that polymerisation takes place entirely at -196°C and not at all while thawing; the second group concluded that polymerisation under the beam takes place only partly at -196°C and partly after irradiation during the thaw, at the phase transformation; and the third group consider that the reaction takes place only at the temperature of the phase transformation and does not take place at all at -196°C. Further studies are obviously necessary in order to reach agreement.

Let us first of all consider the question of why irradiation leads to polymerisation in a solid. Irradiation in a solid (as in a liquid or gas) leads to the production of free radicals, electrons, and ions, which naturally may act as the initial centres for the development of chain polymerisation. In a solid, however, all these particles have a very low mobility (the electrons have a low mobility since they may be captured fairly rapidly by suitable traps). This was confirmed by direct experiments in which the monomers were replaced by substances incapable of undergoing polymerisation. The concentrations of free radicals here could be measured directly by the EPR method. It was found that the concentration of free radicals remains unchanged with time, both at -196°C and also with increase in temperature up to the temperature of the corresponding phase transformation, or, in the absence of such a transformation, up to temperatures comparatively close to the melting point. Under these conditions free radicals recombine rapidly and disappear.

Thus as the temperature of the phase transformation is approached, the mobility of the free radicals increases very rapidly. The same is true of electrons. Buben and Nikol'skii [70] in our Institute observed that specimens previously irradiated at -196° emit light at all phase transformations as the temperature is raised but emit almost no light in the intervals between the phase transformations. This takes place so clearly that they put forward this method (radiothermoluminescence) as an extremely effective and simple method for determining the temperatures of all the phase transformations. It is evident that the electrons captured in various types of trap are liberated and recombine with ions at the temperatures of the phase transformations. An interesting feature is that the phase transformation makes the electrons mobile. It is clear that the sudden rearrangement of the atoms at the phase transformation may create conditions favourable for diffusion processes and for processes of electron transfer.

It is therefore natural that the polymerisation of monomers, initiated by free radicals, ions, and electrons formed on irradiation, will take place particularly readily in the regions of a phase transformation.

It is thus difficult to suppose that polymerisation may take place at temperatures below the phase transformations in solid monomers after irradiation. However, polymerisation directly in the beam can in principle occur at any temperature, no matter how low, since the free radicals, ions, and electrons are produced in a "hot state" so that they may bring about initiation of the growth of the polymer chain. Theoretically, therefore, the possibility of polymerisation at extremely low temperatures is not excluded.

Here, however, it is necessary to make allowance for another feature. If the growth of the polymer chain is to take place rapidly with an activation energy $E = 0$, the monomer molecule being attached must be suitably placed, relative to the terminal radical or ion of the growing polymer chain. In phase transformations, when the molecules can move, this orientation may take place readily. At lower temperatures in the solid, the appropriate orientation takes place with difficulty so that the polymerisation appears to be associated with a fairly high activation energy. In each unit stage in the growth of the polymer chain, however, energy amounting to 14–20 kcal mole^{-1} is liberated. This energy is sufficient to ensure mobility of the neighbouring monomer molecule, that is, to orientate it into the required position. Thus in principle, reaction without activation energy is possible no matter how low the temperature.

Finally, one other important feature must be noted. Polymerisation is accompanied by an increase in the density of the substance, since the distance between the carbon atoms in two neighbouring molecules of the monomer C=C C=C C=C is greater that that in the polymer C–C–C–C–C–C–. Thus the polymer chain developing in the monomer is elongated. In the solid state at low temperatures where there are no phase transformations, the contraction of this chain is very difficult. The chain is frozen in the solid monomer. The elongated molecule may thus be thermodynamically unstable. Polymerisation in the beam is then impossible at low temperature.

It is not excluded that for monomer molecules situated along defects, for example, on the surface of fine crystallites, reaction with contraction of the resulting polymer chain may have a fairly high probability, or at least a probability which is immeasurably greater than that in the bulk. This may be the reason for the so-called "limiting" of the yield of polymer under the beam, observed by Kargin and coworkers[71]. "Limiting" of the yield of polymer is observed from liquid nitrogen temperature to the phase transformation temperature, the maximal yield under the beam being measured in percentages of the total concentration of original monomer (gradually increasing with the temperature of irradiation), whereas Barkalov and coworkers[66] have shown that the "limitation" of the polymer yield is removed by irradiation at the temperature of the phase transformation and above, that is, here the polymerisation may take place throughout the entire volume.

Let us now turn to the most important problem of how the chain propagation reaction in the solid phase can take place with zero activation energy.

Polymerisation processes in the liquid phase, which have been fairly well studied, are of two kinds.

1. Radical Polymerisation

Radical polymerisation occurs under the influence of free radicals A$^{\cdot}$, obtained either by irradiation with light of appropriate wavelength or by the spontaneous decomposition of traces of peroxide mixed with the liquid monomer or its solution:

$$A^{\cdot}+C{=}C \rightarrow A{-}C{-}C^{\cdot},$$
$$A{-}C{-}C^{\cdot}+C{=}C \rightarrow A{-}C{-}C{-}C{-}C^{\cdot}, \text{ etc.}$$

For radical polymerisation in the liquid phase the activation energy of chain growth amounts to 3–5 kcal mole^{-1}. There are no grounds for considering that in the solid this energy can be equal to zero. Radical polymerisation therefore cannot explain the temperature dependence of the reaction rate which we observed, if it were to reflect accurately the course of the reaction under the beam. Closer examination of the suggestion that energy is liberated at the moment a chain grows one unit shows that it cannot explain the fact that the activation energy is equal to zero or the production of long purely energetic polymerisation chains.

2. Ionic Polymerisation

This type of polymerisation takes place in particular under the influence of the acids XI. Ionic polymerisation can be represented schematically:

$$I^{+}+C{=}C \rightarrow I{-}C{-}C^{+}, \quad \text{chain initiation}$$
$$I{-}C{-}C^{+}+C{=}C \rightarrow I{-}C{-}C{-}C{-}C^{+}, \quad \text{chain propagation}$$
$$I{-}C{-}C{-}C{-}C^{+}+C{=}C \rightarrow I{-}C{-}C{-}C{-}C{-}C{-}C^{+}, \text{ etc.}$$

Despite the large number of ionic polymerisation processes, the mechanism of ionic polymerisation is insufficiently clear. It is suggested that the $C{-}C^{+}$ ion is accompanied by a counter-ion Z, so that it is correct to represent the terminal group of the growing polymer in the form $I{-}C{-}C{-}C{-}C^{+}\ Z^{-}$ + C=C. When the next monomeric molecule is attached, the positive charge is transferred to the terminal carbon atom of the polymeric radical formed. The counter-ion moves simultaneously to the same carbon atom $I{-}C{-}C{-}C{-}C^{+}\ Z^{-}$.

In a liquid medium this movement is difficult, particularly if the Z^{-} ion is solvated, and this explains the activation energy (~3000 cal mole^{-1}) for ionic polymerisation. Without these complicating features (the presence of the counter-ion, solvate sheaths, etc.), for example, if the polymerisation took place in a vacuum, the actual process of attachment of a monomer with "overflow" of electrons, and hence the movement of the positive charge along the growing carbon chain, would probably take place without any activation energy. Justification for this suggestion may be provided by the experiments of Tal'roze[72] in the Institute of Chemical Physics and of Stevenson[73] in the USA, who observed various reactions of ions with molecules in a vacuum, in the chamber of a mass spectrometer. It was found that for almost all exothermic reactions of this type the activation energy is zero. Moreover, American[74] and Canadian[75] workers have recently shown that in the ion sources of a mass spectrometer at comparatively high pressures, ionic polymerisation reactions take place to give chains consisting of up to 8 units, with an activation energy almost equal to zero. In solutions, however, ionic reactions always require an activation energy because of the presence of solvate sheaths and interaction with the ions of opposite charge. This might explain the existence of activation energy in the liquid phase and its absence in the solid phase.

In a solid, particularly at low temperature, irradiation with fast electrons or γ-rays, in my opinion, produces a situation which is much closer to the conditions of experiments in the chamber of a mass spectrograph than to the conditions of chain growth in the liquid phase. Here, two features are important. The first is the production, in the solid or in the liquid under the influence of ionising radiation, of secondary electrons with an energy of 10–30 V. These electrons move out from the ion to distances which are considerably greater than the radius of the influence of any existing coulombic forces. They are then captured by an impurity or trap of some sort. The difference between the liquid and the solid (without the phase transformation) is that in the liquid (and also in the phase transformation), the mobility of the ion or the electron combined with the trap is sufficient to ensure rapid approach of the ion and electron with the formation of an ion pair. As we have already noted, the electrostatic forces holding this pair together prevent the growth of the ionic polymer chain without activation. In the solid, however, particularly at low temperature, both the ion and the electron captured by the trap are almost immobile, so that here, as in the chamber of the mass spectrograph at low pressures, the ion may bring about growth of the polymer chain without any activation energy.

A second possibility is that a comparatively fast electron with an energy of ~ 10–30 V geometrically does not go anywhere, but enters the semi-conductivity band and with the charge of the ion forms an electron–hole pair, which may exist for a fairly long period in the form of an exciton, moving in the solid with almost no resistance. The moving particle may then bring about rapid polymerisation. The polymer chain will thus be as it were the track of the motion of the exciton, which is naturally retarded by the necessity for movement of the carbon atoms of the polymer chain, corresponding to hundredths of an Ångström unit. In this instance the rate of movement of the exciton, and the rate of growth of the polymer chain, have values of $\sim 10^5$ cm s^{-1}. Chain termination will be determined by disappearance of the exciton.

As we saw above, until recently all experimental data indicated that the polymerisation of a number of monomers takes place completely or for the most part directly under the beam at low temperatures down to -196°C. Recently, workers in our Institute[76], Abkin[77] in the Karpov Physical Chemistry Scientific Research Institute, and Magat in France began experiments to study polymerisation at liquid helium temperatures. It has already been found that after irradiation at the temperature of liquid helium, the monomers after de-freezing give a polymer in yields close to those observed with irradiation in liquid nitrogen. Here also, however, we are still left with the problem of whether the resulting polymer is produced during thawing.

If polymerisation directly at 4.2°K were firmly established, the only explanation would be the possibility of energetic polymerisation chains, and this would require the introduction of essentially new theories into chemical kinetics, for example, the introduction of the exciton hypothesis. This might open a new page in kinetics.

As we have seen, however, new experiments which contradict this suggestion have recently been carried out. They lead to the conclusion that polymerisation of acrylonitrile under the beam does not take place at -196°C. If future confirmatory experiments by all workers show that this is indeed so, at first sight all this will naturally seem much more trivial. The state of a substance in a phase transformation is analogous to the liquid state or to the state of the solid monomer close to the melting point.

If we think carefully, however, the situation here is not so simple either. Thus in the irradiation of acrylonitrile and formaldehyde, on going from the liquid to the solid monomer, that is, at a temperature only just above the freezing point, the reaction rate in the solid state is greater than that in the liquid state by a factor of 25 for the first and by a factor of 100 for the second. It must be remembered that there are also instances, for example, the radiation polymerisation of HMCTS, when almost no reaction takes place in the liquid phase on irradiation, whereas in the region of the freezing point the rate of conversion immediately reaches very high values, gradually decreasing with further decrease in temperature. Many other similar facts could be cited.

Thus the solid state may in many instances facilitate polymerisation. It is often said that in the solid state intermediate polymeric species may be produced in the form of chains of monomer molecules with correct angular orientation relative to one another, close to that corresponding to the disposition of the C atoms in the polymer chain. In other words, we have as it were the formation of characteristic "polymonomeric" complexes, preceding the polymerisation and facilitating its development after initiation, when one of the monomer molecules is ionised. This situation cannot be realised in a readily mobile liquid monomer. As noted by Kargin[78], in the solid state close to the melting point or in a phase transformation where limited mobility is possible, the most favourable conditions are created for optimal mutual arrangement of the molecules and the production of this type of association. This hypothesis also, however, has not yet been confirmed by direct experiment.

Moreover, another important feature must be noted here. Until now no direct measurements have been made of the rate constant for chain growth at the temperatures of phase transformations (in particular close to the melting point). Thus basically we do not know whether chain growth takes place here with or without activation energy. It must be borne in mind that correct arrangement of the monomer molecules does not in itself eliminate the activation energy, which should then be partly the same as that for the liquid phase (since in the liquid phase the molecules "select" the reaction path corresponding to the lowest activation energy). If the activation energy close to the phase transformations and at the melting point is to be lower than that in the liquid phase, or in the limit equal to zero, we require not only correct arrangement of the monomer molecules, but also the formation of appropriate "polymonomeric" complexes. A fairly wide range of phenomena are now known, in which complex formation may facilitate a reaction considerably, not only as a result of an increase in the pre-exponential term, but also as a result of a decrease in the activation energy. It is possible that on appropriate initiation, almost instantaneous transformation of the "polymonomeric complex" into a polymer chain may occur.

In conclusion I would like to describe some quite different experiments which also indicate, however, that extremely rapid polymerisation processes take place even in the absence of any special chemical chain initiators. Dremin in our Institute has developed an extremely interesting method of studying chemical reactions and phase transformations under the influence of shock waves which are excited using explosives and are propagated through

the solid monomer. Pressures varying from 10 000 to hundreds of thousands of atmospheres are produced in the front of the shock wave. It has been found possible to obtain much information on chemical transformations from the form of the shock front. Dremin has recently extended this method considerably by finding a technique for preserving specimens subjected to the action of the shock wave without allowing their breakdown by the action of the wave. In addition to providing the information obtained by studying the shock front passing through the starting material being studied, this has made possible direct observation of the transformations which occur in it.

A number of results have already been obtained by this method and published. Here, however, I shall mention only the polymerisation processes studied by this method by Barkalov, Gol'danskii, Dremin, Tal'roze, Yampol'skii, and their coworkers[79,80]. It was found that extensive polymerisation of many monomers takes place in the solid state under the influence of a shock wave. Study of the form of the front shows that the polymerisation process takes place in the front of the shock wave in a time interval less than 10^{-8} s. The calculated temperature of the monomer in the shock wave does not exceed 200–300°C. We know that almost no polymerisation takes place at these temperatures in the absence of initiators. We may also note that the yield of polymer remained unchanged when the monomer was cooled to liquid nitrogen temperature, so that we are here dealing with a pressure pulse. Thus the chief role in the polymerisation is played by pressure. The curves giving the form of the shock front indicate that this extremely rapid polymerisation takes place when the pressure in the shock front reaches a value at which the density of the monomer becomes close to that of the polymer under ordinary conditions. This is natural, since at this density the distance between the carbon atoms in the C=C C=C monomer becomes almost equal to the distance between two C atoms in the polymer C–C–C–C. Here, however, the movement of electrons from the C=C C=C groups in the monomer into the C–C–C–C groups in the polymer apparently does not require any activation energy when initiation occurs because the shock wave reduces the marked friction in the specimen.

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THE INFLUENCE OF COORDINATION ON THE REACTIVITY OF ORGANOMETALLIC COMPOUNDS

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I. INTRODUCTION

In attempting to answer the question implied in the title, it must first be recognised, as do Dewar and Thompson [1], that estimates of reactivity generally follow two main directions on the basis of: (a) different charge densities, bond orders, polarisability, etc.; or (b) a different in the energies of the reactants and of the transition state. From the standpoint of strict kinetics, only the second approach is legitimate. All constructs which ignore transition states are incorrect in principle. However, the second approach encounters serious theoretical difficulties [1], and in organometallic chemistry only the first has yet been practical, the approach of coarse correlations, giving only an approximate idea of the comparative reactivity of various compounds. The present work is not an exception in this sense.

The various reactivity series for the metal alkyls [2] are widely recognised as too generalised. It is evident that such series cannot be applied to reactions which differ in nature and in mechanism. In speaking about the comparative reactivity of organometallic compounds in a series of different reactions these reactions must be divided into groups similar in some features which play a decisive part. Practice shows that to a first approximation two types of organometallic reaction must be distinguished — additions to multiple bonds and substitutions. Neglect of these simple considerations necessarily leads to confusion both in the comparative evaluation of the reactivity of different compounds, and also in the evaluation of the influence of different complex-forming media on the activity of the same compound. To avoid this widespread error mainly substitutions will be considered.

Furthermore, following the now commonly accepted point of view, it must be assumed that in most such reactions the breaking of the metal–carbon bonds is heterolytic

for the rather active metals (Li, Mg, etc.). The energy of the heterolytic breaking of a non-ionic bond $A-B \rightarrow A^+ + B^-$ is greater than the energy of its homolytic dissociation, since to bring about such breaking it is necesary to do additional work in polarising the bond[3,4]:

$$D_H = E + I_A - E_B,$$

where D_H is the energy of heterolytic breaking of the bond A–B, E the bond energy, I_A the ionisation potential of A, and E_B the electron affinity of B. Eaborn[4] successfully used this approximation to evaluate the reactivity of different $\rangle$Si–X bonds in heterolytic substitutions of X. The application of this to metal–carbon bonds has apparently not been attempted.

The energy of heterolytic bond-breaking is extremely dependent on the solvolytic capability of the medium. With ionic bonds, solvation is the motive force for the destruction of the lattice during the dissolution of a substance in an ionising medium. With non-ionic, but sufficiently polar, bonds ionisation again cannot be neglected, but the energy of heterolytic breaking of the bond in a strongly solvating medium should obviously be less by some quantity proportional to the solvating ability of the medium, which is connected with the additional polarisation of the bond under the action of the solvent.

With organometallic compounds which contain rather polar bonds (M–C, M–H, M–Cl, etc.) this means that strong solvation should bring about additional polarisation of these bonds. However, the nature of this solvation is important.

Two fundamental types of solvating interaction must be distinguished[5,6]. Firstly, solvation can be a purely electrostatic interaction of the polar molecules of the solvent with molecules of the solute without the formation of any chemical bonds between them. Secondly, solvation can occur through bonds which have a donor–acceptor nature. Finally, there is specific solvation[5]. Electron-deficient cations form coordination complexes with solvents which possess electron-donor atoms; anions tend to form hydrogen bonds using the partially protonated hydrogen atoms of the solvent. In both instances we are concerned with specific solvation. Solvents which do not contain hydrogen atoms capable of forming hydrogen bonds are termed aprotic[5]. They are incapable of the specific solvation of anions but if electron-donor atoms (usually oxygen) are present they form coordination complexes with cations. After the appearance of Parker's review[5], the view became widely accepted that in a polar aprotic solvent medium the nucleophilic activity of anions in bimolecular substitutions (S_N2) of the anion–dipole type is greatly increased.

Among the factors which determine the increase in the reactivity of anions in S_N2 reactions are the following[5-7]: (1) the weak solvation of the anion, which makes it mobile in comparison with a strongly solvated counter-ion: (2) the breakdown of ion pairs (or ionic aggregates) due to the strong solvation of cations with the formation of "free" anions; and (3) the polarisation of a transition state, leading to the separation of the charges.

Most organometallic compounds do not have an ionic structure and do not form independent carbanions in solution. The validity of applying the concepts of the accelerating action of dipolar aprotic solvents on S_N2 reactions of anions to the reactions of organometallic compounds is not so obvious in this connection. It is characteristic that Parker[5] included in his review only certain reactions of alkali enolates having an ionic structure; he did not consider true organometallic compounds.

Tchoubar[6], in referring to the earlier work of Hammett[8], emphasises that an increase in the ionicity of a bond takes place precisely as a result of donor–acceptor interaction and that the characteristics of the medium such as dipole moment, dielectric constant, etc. play only a subordinate part in this increase. The conditions for dissociation into independent ions is here no longer obligatory, however, and Tchoubar in effect did not consider organometallic compounds.

Nevertheless, as will be shown below, the effect of aprotic electron-donor solvents and complex-forming anions in this field of chemistry is pronounced[9] and, with the reservations made at the beginning, of a rather general character.

II. INFLUENCE OF COORDINATION ON THE PHYSICAL PROPERTIES OF BONDS

In the specific solvation of an organometallic cation or of the positive end of a dipole there is a change in the valence state of the metal atom, which is inevitably accompanied by a change in the spatial configuration of the molecule, the interatomic distances, valence angles, etc. Digressing from that, the role which a dipolar aprotic solvent plays in a transition state nevertheless means that coordination facilitates an increase in the ionicity of the bonds in the initial compound. For ionic crystals this principle was formulated and generalised by Pauling[10]. It is supported by many experimental data, most of which relate, unfortunately, to inorganic materials.

A comparison of the quadrupole frequencies of ^{35}Cl in tin tetrachloride (24.296, 24.226, 24.140, and 23.720 MHz) and of the $SnCl_6^{2-}$ anion (15.61–15.73 MHz, depending on the nature of the cation) shows that chlorine is considerably more ionised in the complex anion than in the tetrachloride[11], which is consistent with the Mössbauer spectral data[12]. In the formation of the trimethyltin chloride complex with pyridine the Sn–Cl bond (2.37 Å) is lengthened (2.43 Å), and the complex has a planar configuration of the $(CH_3)_3Sn$ group, while the chlorine and nitrogen atoms are located at the vertices of a trigonal bipyramid[13,14]. The example of dibutyltin dichloride showed that the quadrupole splitting of the γ-transition of ^{119m}Sn depends strongly on the nature of the complex-forming solvent and its mole fraction[15]. It is characteristic that the increase in quadrupole splitting is continued up to a solvent : $(C_4H_9)_2SnCl_2$ molar ratio of 3, that is, even after the formation of an equimolecular complex. The polarisation of the Sn–Cl and Pb–Cl bonds in the formation of complexes of trialkyltin chlorides and trialkyl-lead chlorides with *NN*-dimethylacetamide and *NN*-dimethylformamide, with production of a bipyramidal structure also follows from the infrared and NMR spectra of these complexes[16].

A study of the proton resonance spectra of triethylaluminium, triethylgallium, and their ether addition compounds led Brownstein and coworkers[17] to conclude that in the complexes with ether the metal–carbon bonds were more "antibonding" in comparison with the initial metal alkyls. The decrease in the "electronegativity" of the aluminium atom on going from the trialkylaluminiums to complexes of the $MAlR_4$ type was also noted on the basis of their NMR spectra[18]. It is interesting that the tendency of the aluminium atom in such complexes to coordination is

not exhausted, and when they are dissolved in ether additional coordination with the ether takes place, accompanied by distortion of the AlR_4^- tetrahedron [19].

An increase in the bond length, which is usually associated with an increase in their ionicity [10], also follows from purely structural data. Thus the B–F bond, equal to 1.30 ± 0.02 Å in boron trifluoride is extended to 1.38–1.40 Å in the complexes of boron trifluoride with amines [20]. The bonds of mercury with halogens are lengthened on increasing its coordination number [21].

III. CHEMICAL CONSEQUENCES OF COORDINATION

The marked influence of electron-donor aprotic solvents on the course of various organometallic reactions has been repeatedly noted by many authors; however, the most varied assumptions have been made to explain these observations and until recently there has been no general approach to the appraisal of the role of the complex-forming media. The matter is also complicated by the fact that the same solvent often behaved differently towards different solutes. It is sufficient to mention that the addition of alkyl-lithiums to multiple bonds is often accelerated by complex-forming ethers, which is connected with the increase in the polarity of the C–Li bond in a complex with an ether [22,23], whereas the trialkylaluminium–ether addition compounds add to the alkenes with greater difficulty than the original alkylaluminiums [24]. Grignard reagents give lower yields of addition products with ketones in tetrahydrofuran [25], but they are especially effective in alkylation reactions in tetrahydrofuran [9]. Such behaviour often led to conflicting judgements. It is characteristic, for example, that in the celebrated monograph of Rochow and coworkers [2] it is stated directly that "under the influence of solvation bond polarity is decreased, thanks to the concentration of electrons with the electronegative donor atom of the solvent"†. The authors consider this question in direct association with the decrease in reactivity of the organometallic compounds during a fall in the polarity of the metal–carbon bond. However, analysis of the facts that have been accumulated at present shows this conclusion to be incorrect.

The increase in the polarity of metal–carbon bonds during coordination at the metal atom is confirmed by the acceleration of the heterolytic reactions of substitution and exchange in complex-forming media.

Ziegler [26] notes an increase in the rate of the "normal" Wurtz reaction:

$$RLi + R'X \rightarrow RR' + LiX,$$

in ether in comparison with a hydrocarbon medium and explains this phenomenon by the greater "ionising" ability of the ether. Eastham and Gibson [27] found that the rate of the reaction

$$C_4H_9Li + RBr \rightarrow LiBr + C_4H_9R,$$

is 10^3 times greater in the presence of ether [than in hexane (Ed. of Translation)], which the authors connect with the conversion of the hexameric butyl-lithium into a dimer on coordination with ether. According to Gilman and coworkers, the metallating ability of the alkyl-lithiums is higher in ether than in a hydrocarbon [28] and higher in tetrahydrofuran than in ether [29,30]. Gilman notes that the ease of metallation of fluorene and its analogues by the alkyl-lithiums in various ethers is proportional to the instability of their solutions in the ether concerned, but does not link this effect with a difference in the solvating ability of the solvent.

In recent years it has been found that a sharp increase in the nucleophilic activity of the alkyl-lithiums in substitutions also takes place in the formation of complexes with amines. Thus the complexes of butyl-lithium with *NNN'N'*-tetramethylethylenediamine and 1,4-diazobicyclo[2,2,2]octane metallise not only toluene, but also benzene more readily than butyl-lithium itself [31]; the reaction takes place even at room temperature.

Brown and coworkers [32] explain the increase in the reactivity of alkyl-lithiums in the presence of Lewis bases by a decrease in the degree of association of the initial compound. Actually, these authors showed that in the action of triethylamine on hexameric ethyl-lithium the latter dissociates into three molecules of coordinated dimer. The decrease in the degree of association of alkylmagnesium halides in a strongly solvating medium [33–35] is accompanied by their partial symmetrisation [34].

The general occurrence of a decrease in the degree of association is frequently considered to be the main reason for an increase in the reactivity of organometallic compounds. It is clear, however, that despite their plausibility, these concepts do not satisfactorily explain the nature of the action of the complex-forming media, since solvents capable of coordination markedly increase the reactivity of even those compounds which are monomers themselves (R_2Zn, [36] R_2Cd [37]).

The addition of Lewis bases to organolithium compounds increases their activity also in additions to multiple bonds [22,38–42].

It becomes more and more evident from recent data that the use of strongly solvating solvents accelerates nucleophilic substitutions of organomagnesium compounds. Thus the ease of the "normal" Wurtz reaction:

$$RMgX + R'X \rightarrow RR' + MgX_2,$$

is proportional to the solvating ability of the ether used as the solvent [43]. Whereas in diethyl ether the "normal" Wurtz reaction is brought about only for the allyl, benzyl, and greatly branched tertiary radicals [44], in dimethoxyethane the simplest aliphatic radicals readily undergo it [43].

According to Normant [45] the solvating ability of the medium ("basicity", in the expression of the author) is one of the deciding factors which determine the possibility of Grignard reactions with the halogen derivatives of alkenes and alkynes. The condensation of Grignard reagents with halogenoacetylenes:

$$RMgBr + Br{-}C{\equiv}CR' \rightarrow R{-}C{\equiv}C{-}R' + MgBr_2,$$

takes place only in a medium of hexamethyltriamidophosphate [hexamethylphosphoric triamide (Ed. of Translation)], but in less solvating solvents (ether or tetrahydrofuran) it does not occur. On the other hand, the Wurtz reaction with participation of unsaturated Grignard reagents and propargyl bromides occurs smoothly even in tetrahydrofuran [45].

† Reference 2, page 24 states: "Normally the effect of solvation is to decrease bond polarity by contribution of electrons from the electronegative donor atom of the solvent (the oxygen of ether, etc.) to the metal, but solvolytic dissociation into ion pairs also may occur". (Ed. of Translation).

Whereas a Wurtz reaction between heptynylmagnesium bromide and propargyl bromide catalysed by copper(I) chloride takes place in 115 h at 37° in diethyl ether, it needs only 1.5 h at the same temperature in tetrahydrofuran. The times for the analogous reaction with 1-chloropentyne are 65 h in ether and 1 h in tetrahydrofuran[46].

For the usual Grignard reagents in diethyl ether an exchange of radicals of the type:

$$RMgX+R'X \rightleftarrows R'MgX+RX,$$

is not characteristic and is observed only in certain specific instances. In a medium of the more solvating ethers even the simplest aliphatic and aromatic halides also take part in the exchange reaction[47-49]. The degree of exchange in the system n-$C_5H_{11}MgBr$ + CH_3I (0°, 1 h) in diethyl ether, diethoxyethane, ethoxymethoxyethane, diglyme, tetrahydrofuran, and dimethoxyethane, is respectively 5.7, 6.6, 12.7, 15.8, 17.5, and 38.5%. Aromatic iodides in dimethoxyethane medium exchange 52-75% after 3 h, giving the corresponding arylmagnesium halides[47].

Significantly, the completely unsolvated organomagnesium compounds which are obtainable in hydrocarbon medium[50] react with alkyl halides by a free radical mechanism[51]; the reaction products RMgX + R'X here are the products of the conversion of the free radicals R' and R''. The very nature of the breaking of the C–Mg bond (homolytic or heterolytic) in RMgX + R'X systems is thus determined by the nature of the solvent.

The accelerating action of electron-donor aprotic solvents appears especially clearly in metallating reactions. The simple replacement of ether for tetrahydrofuran makes the formation of Iotsich complexes strongly exothermic and rapid[9]. Metallation by alkylmagnesiums takes place very readily in hexamethyltriamidophosphate[52,53], where fluorene, indene, triphenylmethane, etc. are smoothly metallated. The usual Grignard reagents metallate fluorene only at 130°, but triphenylmethane is not metallated at all. Evidently, hexamethyltriamidophosphate ("hexametapol") $[(CH_3)_2N]_3PO$ is still the best solvent for metallating reactions: other complex-forming solvents are inferior to it in accelerating action[53].

Kinetic data on the metallation of hex-1-yne by ethylmagnesium bromide[33,54] are somewhat contradictory. On the one hand, replacing ether by tetrahydrofuran somewhat accelerates the reaction, but at the same time a reaction which is bimolecular in ether becomes termolecular[33]. However, in the presence of a tenfold excess of the hexyne the rate of its metallation by ethylmagnesium bromide falls with increase in the solvating ability of the ether in which the reaction is carried out[54]. It is possible that this exception from the general rule is due particularly to the presence of a large excess of acetylene, which changes the mechanism of the reaction.

It has been repeatedly noted that many alkylations of element–halogen bonds by Grignard reagents in a medium of tetrahydrofuran take place more rapidly and with better yields of organoelemental compounds than in ether[55-58]. This phenomenon, however, is frequently explained by the greater dissolving power of tetrahydrofuran or the possibility of working at a higher temperature. In reality, these factors hardly seem decisive; the main reason for the accelerating action of tetrahydrofuran is that in relation to a Grignard reagent it is a better complex-forming agent than ether. Really, dialkylthallium halides are alkylated to trialkylthalliums only by organolithium compounds and the usual Grignard reagents (in ether) are unsuitable for this purpose. In tetrahydrofuran the reaction takes place readily even at 0–5°; for example, triethylthallium is thus obtained[9,59]:

$$(C_2H_5)_2TlCl+C_2H_5MgBr \xrightarrow[0-5^\circ]{THF} (C_2H_5)_3Tl.$$

The sterically hindered alkylation of trichlorosilane by 1-naphthylmagnesium bromide in ether does not give any tri-(1-naphthyl)silane[60]: in tetrahydrofuran the latter is obtained with a yield < 30%,[33] and in an even more solvating ether – dimethoxyethane – the reaction proceeds under mild conditions and gives trinaphthylsilane with a yield > 70%:[9]

$$HSiCl_3+3\alpha\text{-}C_{10}H_7MgBr \xrightarrow{\text{dimethoxyethane}} (\alpha\text{-}C_{10}H_7)_3SiH+3MgBrCl.$$

The relatively inactive phenylethynylmagnesium bromide alkylates chlorotrimethylsilane only at 100° (after removal of ether)[60]; however, in tetrahydrofuran, and even more in dimethoxyethane, the reaction is exothermic at room temperature and the yields of trimethyl(phenylethynyl)silane are 47 and 77% respectively[9]:

$$(CH_3)_3SiCl+C_6H_5C{\equiv}CMgBr \rightarrow C_6H_5C{\equiv}CSi(CH_3)_3+MgBrCl.$$

In using dimethoxyethane as a solvent phenylmagnesium bromide can be used successfully instead of phenyl-lithium for obtaining pentaphenylantimony[9]:

$$(C_6H_5)_3SbCl_2+2C_6H_5MgBr \xrightarrow{\text{dimethoxyethane}} (C_6H_5)_5Sb+2MgBrCl.$$

Recently Ingold[61] reported that in the presence of dimethyl sulphoxide dialkylthallium halides are alkylated even by organomercury compounds.

As already noted, with alkyl-lithiums the coordination at the lithium atom facilitates both substitutions and also addition to multiple bonds. With organomagnesium compounds things are otherwise. Strongly solvated Grignard reagents give worse yields of addition products in reactions with ketones[25] and nitriles[62]; in some other instances only slight influence of solvation was observed[63].

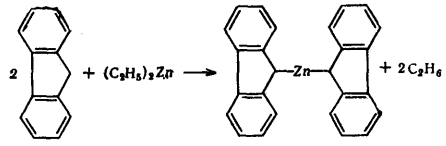
With organozinc compounds even such "classical" dipolar aprotic solvents as dimethylformamide and dimethyl sulphoxide can be used as strongly solvating media. In a non-complex-forming (hydrocarbon) medium diethylzinc hardly metallises phenylacetylene at all, whereas in hexamethyltriamidophosphate the reaction is violent[36]:

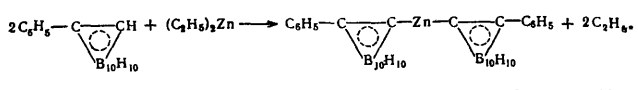
$$2C_6H_5C{\equiv}CH+(C_2H_5)_2Zn \rightarrow (C_6H_5C{\equiv}C)_2Zn+2C_2H_6.$$

The complex-forming solvents are arranged in the following series according to their accelerating action on this reaction (under the formula is given the time needed for half the theoretical amount of ethane to be liberated, in seconds)[36]:

$$\underset{\infty}{[(CH_3)_2N]_3PO} > \underset{200}{(CH_3)_2SO} > \underset{270}{(CH_3)_2NCHO} > \underset{7200}{CH_3OCH_2CH_2OCH_3} > \underset{\infty}{n\text{-}C_7H_{16}}.$$

Use of hexamethyltriamidophosphate allows even fluorene and phenylbarene to be readily metallised by diethylzinc:





The influence of electron-donor solvents on the reactivity of diethylcadmium is as perceptible again[37]. The

time for the half liberation of the theoretical amount of ethane in the reaction of diethylcadmium with phenylacetylene is 3 h 50 min in dimethylformamide, 1 h in dimethyl sulphoxide; it is characteristic that the difference in the accelerating action of these solvents for diethylcadmium is more significant than for diethylzinc. Whereas in ether diethylcadmium does not metallate phenylacetylene, in the presence of *NNN'N'*-tetramethylethylenediamine the reaction is almost explosive[37].

It was noted earlier[9] that no sharp distinction can be made between the solvation of an organometallic compound by donor–acceptor interaction with the solvent and the formation of stable complexes of the "reverse onia" type. Actually there are arguments in support of the idea that the reactivity of such complexes is higher than that of the original organometallic compounds[64]. Whereas neither potassium hydride nor butyl-lithium separately metallates alkylbenzenes their complex with one another $K[LiH(C_4H_9)]$ does so readily[65]. The alkylation of element–carbon bonds by trialkylaluminiums takes place more readily when the latter are bound in complexes with ethers or amines[66,67]. This also holds for the metallating ability of complexes of the $MAlR_4$ type in relation to alkynes: whereas trialkylaluminiums (except for triphenylaluminium[68]) add to the triple bond of alkynes the $MAlR_4$ complexes metallate them[69]. The complexes of alkylaluminiums with tertiary amines behave similarly[70].

It is significant that the addition of potassium chloride to unreacted mixtures of trimethylaluminium and silicon tetrachloride leads to the formation of tetramethylsilane[64]. The use, not of alkylaluminiums, but their complexes with alkali metal halides for the synthesis of organometallic compounds allows the process to be made more selective and with greater conversion of the alkyl groups[71,72].

The exchange of labelled mercury in $RHgX + Hg^*X_2$ systems is catalysed by halide anions and acetate ions, which form coordination complexes with the original organomercury compounds[73,74].

In the presence of iodide anions the breaking of Hg–C bonds in organomercury compounds with elemental iodine becomes a heterolytic reaction[75-87]. Beletskaya and coworkers suggested[76] that the decisive step in this exchange mechanism can be the formation of a complex of the organomercury compound with the iodide anion, which leads to the "relaxation" of the Hg–C bond. They later demonstrated the existence of such complexes with phenylmercury(II) chloride during a study on nucleophilic assistance in protodemercuration reactions[79]. The mechanism of assistance in reactions with multicentre transition states, with allowance for the effect of the medium, has also been considered by Dessy and Paulik[7].

It is evident that here the authors are dealing with the reduction of the energy of the heterolytic breaking of a metal–carbon bond under the influence of coordination at the mercury atom.

It has already been shown above that extension of the thesis of an increase in nucleophilic activity of organometallic compounds during complex formation in substitutions to additions can lead to erroneous conclusions. Such an ambiguous effect of coordination also appears in oxidations, carbonations, and some other reactions. Thus the coordination of diphenylmagnesium by ethers facilitates its oxidation by atmospheric oxygen[80], yet the rate of oxidation of a 2-phenylbis(biphenylene)alkylsodium falls sharply as the solvating ability of the solvent is increased[81]. Evidently, the strong specific solvation facilitates carbonation: alkali metal acetylides are smoothly carbonated (under pressure) in dimethylformamide[82] but hardly at all in ether. The carbonation of pentafluorophenylmagnesium halides in tetrahydrofuran gives pentafluorophenylbenzoic acid in 67% yield[83]. The same Grignard reagent in ether does not react with ethylene oxide but in tetrahydrofuran it smoothly forms 2-pentafluorophenylethanol (yield 82%)[84]. However, the information available about the influence of coordination on the ease of addition is clearly insufficient for any generalisations.

Summarising, the following general conclusions can be drawn:

1. Dipolar aprotic solvents form complexes of the donor–acceptor type with organometallic compounds, identical in many respects with the complexes of these compounds with anions ("reverse onia").

2. Both here and elsewhere there is an increase in the polarity of the bonds of a metal with more electropositive partners, including carbon, which lowers the energy of heterolytic breaking of metal–carbon bonds and makes a little-solvated carbanion (or carbanion end of a dipole) exceptionally active in heterolytic exchanges.

3. The influence of coordination on the course of additions is ambiguous, since here two opposing factors operate: (a) an increase in the nucleophilic nature of the metal–carbon bond; (b) a hindering of complex formation with an unsaturated compound, which prevents the necessary increase in the electrophilic nature of the multiple bond in the transitional state.

IV. FACTORS WHICH DETERMINE THE CHARACTER OF COORDINATION

The extent of the changes referred to above depends on the complex-forming (solvating) ability of the molecules of the donor in relation to a given organometallic compound. The problem of the methods for evaluating this ability is still not completely clear, however. From a comparison of given series of solvating solvents it becomes clear already that in relation to different compounds the different series of solvating abilities agree with one another only in the most general features, while differing considerably in details. It is quite evident, as Hamelin noted[85] for organomagnesium compounds, that interpretation only in terms of the basicity of the donor towards a proton is impossible since there is usually no direct correlation between the basicity of a ligand and its complex-forming ability in most of the examples considered. In relation to trialkylboron compounds the complex-forming ability of different amines ($NH_3 > EtNH_2 > Et_2NH > Et_3N$) is the reverse of their basicity in water ($NH_3 < EtNH_2 < Et_2NH < Et_3N$)[86]; the ability of aluminium hydride to coordinate decreases in the following series of solvents: tetrahydrofuran > Et_3N > > EtOEt.[87] Unlike tetrahydrofuran and dimethoxyethane, the strongly basic triethylamine has no significant accelerating action on the exchange[48,49]:

$$RMgX + R'X \rightleftarrows R'MgX + RX$$

Different ethers which differ little in their "basicity", differ markedly in their ability to coordinate with ethylmagnesium bromide[34] and in their accelerating action on the reaction of organomagnesium compounds (see above).

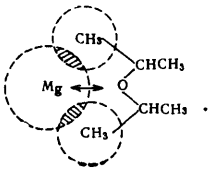
The examples given suffice to show that the basicity alone of a donor in relation to a proton is not a deciding

factor. Because of this, the use of the term "basicity", even with a series of reservations, is undesirable, since it creates the danger of misinterpretation. It is more correct to speak of the complex-forming ability of the donor (corresponding to the solvating ability of a medium) or of the affinity of a ligand for a particular cation or molecule, as is done, for example, by Ahrland and coworkers[88].

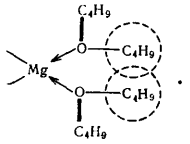
The non-correspondence between the proton-basicity of a donor and its coordination capability is due to a combination of factors, which must be considered in greater detail.

From the viewpoint of inductive effects tetrahydrofuran and diethyl ether should be donors of approximately equal strength; the fact that tetrahydrofuran is in reality a better complex-forming agent is usually explained by the absence of steric hindrance in coordination by this solvent[89].

The importance of the steric requirement in coordination has been stated repeatedly. Brown and coworkers[90] distinguish two types of steric hindrance during coordination — *B*- and *F*-strains. In the first the steric hindrances arise because of degree of branching close to the donor atom of the ligand; thus Hamelin[34] explains, for example, the low "basicity" of di-isopropyl ether in relation to a Grignard reagent:



In the second, equivalent to the *F*-strain of Brown and coworkers, solvation is hindered by the general steric hindrance of the ligand molecules arising during coordination[34]:



It is to be expected that the relation between the *B*- and *F*-factors will depend significantly on the dimensions of the metal atom: an increase in its covalent radius should intensify the role of *F*-strain and reduce the influence of *B*-strain. Clearly it is also necessary to consider the obstructions created by the replacing groups at the metal atom.

As well as the steric requirement of the substituents at the atoms of the donor and metal, the electron-donor properties of these substituents must be considered. Depending on the character of the substituent the donor–acceptor properties of the central atom can change within wide limits. Whereas, for example, trimethylantimony is a Lewis base, perfluorotrimethylantimony contains a coordination-unsaturated antimony atom capable of adding pyridine[91]. The feeble donor properties of diphenyl ether are undoubtedly due to the interaction of the unshared electron pairs of the oxygen with the π-electrons of the phenyl rings; in the absence of steric hindrance aryl derivatives of metals form, as a rule, more stable coordination complexes. Among recent studies mention may be made of the work of Noltes and van der Kerk[92], who showed that diphenylzinc forms coordination complexes more readily than dibutylzinc.

The replacement of hydrogen by a methyl group directly at a donor atom of a ligand significantly increases the ability of the latter to coordinate. In its capability for coordination dimethyl ether should significantly surpass diethyl and the higher ethers. This is also facilitated by the favourable steric conditions with the former. Actually, the heat of formation of the ether addition compound $(CH_3)_3Al{-}O(CH_3)_2$ is 19 kcal × × mole^{-1} [93] whereas that for the complex $(CH_3)_3Al{-}O(C_2H_5)_2$ is 11.2 kcal mole^{-1}.[94] An even more marked difference in the solvating ability of dimethyl and diethyl ethers appears in the formation of the naphthalene negative ion from sodium and naphthalene[95]: diethoxyethane has always been found to be a much less suitable solvent than dimethoxyethane[49,96].

A very important factor, which favours coordination, is the bidenticity of a donor and the possibility of forming a five-membered ring. Usually, bidentate ligands give more stable complexes and to a greater measure bring about all those changes mentioned above. Coordination complexes with ligands of this type have also been described for many organometallic compounds — for derivatives of beryllium[97], magnesium[98,99], zinc[100], cadmium[101], and boron and aluminium[24]. It is characteristic that dimethylcadmium with unidentate donors (tetrahydrofuran, pyridine) gives liquid 1 : 1 complexes which dissociate into the components even at low temperature, whereas analogous complexes with *NNN'N'*-tetramethylethylenediamine, 2,2'-bipyridyl, and 1,10-phenanthroline are solid and stable[101]. When the initial organometallic compound is associated (R_2Be, R_2Mg), coordination with bidentate ligands leads to the formation of monomeric complexes to a greater degree than for other complex-forming agents, which must also make a contribution to the general nucleophilic nature of the M–C bond. Thus, dimethylberyllium forms monomeric complexes with dimethoxyethane, *NNN'N'*-tetramethylethylenediamine, etc.[97]; the complex of dimethylmagnesium with this diamine can be distilled[98,99]. Unfortunately in studying the conditions for the formation of such complexes and their stability, most authors do not give any information about the interesting problems of their reactivity in comparison with that of the initial compounds.

Allowance must be made for the fact that the tendency of various metals (as ions or parts of molecules) to complex formation under equally severe conditions also depends on the nature of the donor atom of the ligand[88]. Most acceptor-metals form the most stable complexes when the donor atom belongs to the Second Period of the Periodic System (N, O, F). However, some metals (for example, mercury) give more stable complexes with elements of later periods (P, S, B, etc.). Transition metals such as cadmium, thallium, lead, and bismuth occupy an intermediate position and their affinity for one or another type of ligand depends on the specific conditions, including the nature of their environment. Boron is adjacent to these elements; characteristically[83,102], whereas the activity of the donors in relation to trimethylboron falls in the sequence N > P > As, in relation to borane (BH_3) this sequence alters (N < P ≫ As)‡.

Evidently information on the stability of complexes and on the affinity of ligands for different Lewis acids (including ions and polar molecules) can be used, with some limitations, also for evaluating the change in polarity of bonds and reactivity during coordination.

‡ $(CH_3)_3N$, $(CH_3)_3P$, and $(CH_3)_3As$ were used throughout.

With increase in the atomic number of the metal within the limits of Groups IIb–V there is an increase in the polarisability of the atomic core, which as a whole leads to an increase in the polarisation interaction between the atoms, and consequently to a decrease in the ionicity of the bond. It could evidently be expected that the relatively strong polarisation interaction would also level out to some extent the effect which is brought about by coordination. When the metal atom exhibits sufficiently mobile d-electrons (for example, atoms of metals of type $d^{10}s^2$) and the donor-atom has vacant d-orbitals, the d_π–d_π dative interaction between the atoms of the metal and the donor is an additional factor stimulating the formation of a complex. A consequence of this is, for example, that with increase in the atomic number of the metals in the zinc subgroup there is a rise in the tendency of their compounds to form complexes with derivatives of phosphorus, sulphur, and other elements having vacant d-levels.

It is evident that the reactivity of organocadmium and organomercury compounds will increase under the influence of complex-forming agents containing phosphorus and sulphur to a greater extent than that of the corresponding compounds of magnesium and zinc.

Hence at present it is possible to draw only the following tentative conclusions.

1. The influence of complex formation on the nucleophilic reactivity increases with effective charge at the nucleophilic atom, which, in turn, depends on the relative affinity of the given ligand for the compound concerned.

2. This affinity depends on: (a) the nature of the metal and of the donor atom of the ligand; (b) steric conditions; (c) the bidenticity of the ligand; (d) the inductive effects created by the substituents at the metal and the donor atom; (e) the Lewis basicity of the ligand; (f) factors which at present still cannot be understood. The action of all these factors may not be concordant, which in theoretical respects greatly complicates the problem of the degree and character of the different solvation effects and coordination phenomena.

3. Ideas about complex formation by metal ions (i.e. concepts from the chemistry of complex compounds) can evidently be transferred to complex formation by organometallic compounds, with definite limitations, and this allows a rough *a priori* appraisal to be made.

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PROGRESS IN THE FIELD OF THE CHEMISTRY OF STEROIDAL HETEROCYCLES

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I. INTRODUCTION

In recent years the attention of investigators has been attracted more and more to a series of new, unusual steroidal compounds in which a cyclopentenoperhydrophenanthrene system is condensed with various heterocycles. The increased interest in the compounds of this class is also due to the fact that the number of known steroidal heterocycles isolated from natural sources is increasing each year. An important place among steroid sapogenins is occupied by compounds with a condensed tetrahydrofuran ring. The study of the structure and properties of the alkaloids of the steroid series which show high physiological activity showed that many of them (solanidine, solasodine, tomatidine, conessine, cevine, rubijervine, etc.) are also condensed heterocyclic systems of the steroid series.

The adding on of heterocyclic rings in different positions of a steroid molecule is effected by the usual, well-studied procedures, widely employed in the chemistry of heterocyclic compounds. The initial substances for the preparation of heterocyclosteroids most frequently are ketones, hydroxymethyleneketones, and other accessible derivatives of steroids.

As was to be expected, the addition of heterocycles to steroids often leads to a change in their physiological activity and the appearance of new, interesting biological properties. For example, the fusion of a pyrazole heterocycle to ring A of the steroid nucleus significantly increases the selectivity of its endocrinological activity. Thus 17α-androstano[3,2-c]pyrazole obtained on the basis of 2-hydroxymethylene-17α-methyldihydrotestosterone is 35 times more active than methyltestosterone as an anabolic agent, exhibiting in this one-quarter of its androgenic activity. This observation served as an impetus for the extension of the investigations in the field of synthesis of steroidal heterocycles, and now we know a large number of steroidal pyrazoles and pyrazolines, isoxazoles and isoxazolines, pyrroles and indoles, pyridines and quinolines, thiazoles, triazoles, etc.

Since the numerous data on the synthesis and properties of the heterocyclosteroids are scattered, this stimulated us to write the present review, in which the main literature published up to the end of 1965 is systematised. It deals with the methods of synthesis and properties of only condensed heterocyclic steroid compounds. The numerous steroid derivatives containing heterocyclic residues are not presented in this review. The authors also do not discuss α-oxides, thio-oxides, lactones, dioxolanes, and other analogous compounds of the steroid series which are described in detail in the literature.

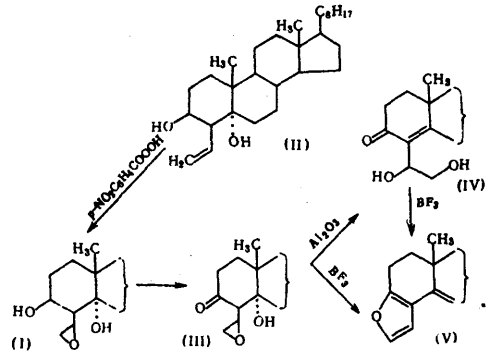
II. STEROIDS CONDENSED WITH FIVE-MEMBERED HETEROCYCLES

1. Synthesis of Furanosteroids

Compounds with a condensed furan ring are found among the natural alkaloids, the mono-, sesqui-, di-, and tri-terpenoids, and also the steroids.

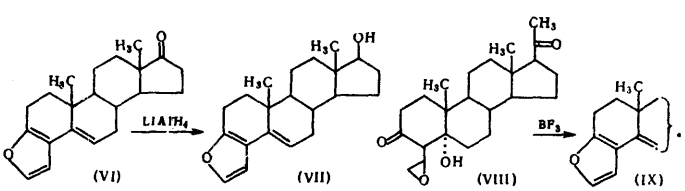
A series of furano-derivatives of cholestane, androstane, and pregnane was recently obtained in good yields by the cyclisation of $\beta\gamma$-epoxyketones of the steroid series in the presence of boron trifluoride–diethyl etherate[1].

Epoxyketols (I) of the cholestane series are obtained from 4β-vinyldiols (II) [2] on reaction with peroxy-acids (for example, p-nitroperbenzoic acid). The reaction proceeds in ether, tetrahydrofuran, or their mixtures:

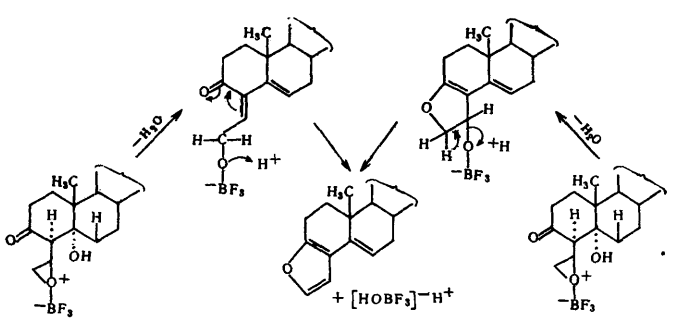


It is noted[1] that the epoxydiol (I) is better converted into the epoxyketol (III) by oxidation with the Jones–Kiliani reagent than by the complex of chromium(VI) oxide with pyridine. The epoxyketol (III) is readily dehydrated in alkaline medium and even during passage through a column of alkaline aluminium oxide it is quantitatively converted into a product with an opened epoxide ring (IV). On treatment with boron trioxide–diethyl etherate, both (III) and (IV) are converted into the furan derivative (V).

By a series of analogous conversions in the androstane series the furanoketone (VI) was obtained, which can then be reduced to the furanotestosterone (VII), and in the pregnane series by treatment of the unpurified epoxyhydroxydiketone (VIII) the corresponding furanoprogesterone (IX) was isolated in 85% yield:



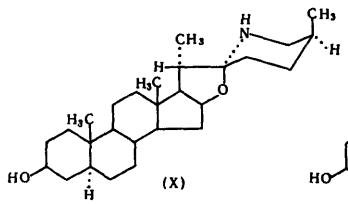
The mechanism of the cyclisation of the furano-derivatives is:



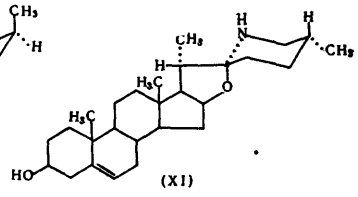
Biological tests showed that the propionate of furanotestosterone (VII) was devoid of androgenic and anabolic activity when administered either subcutaneously or orally[1].

Among the steroidal sapogenins (sarsasapogenin, diosgenin, etc.) an important place is occupied by tetrahydrofuran derivatives in which the heterocycle is condensed with ring D of the steroid in positions 16 and 17. The derivatives which contain the tetrahydrofuran ring are found among the

steroidal alkaloids of the tomatidine (X) and solasodine (XI) type[3]:

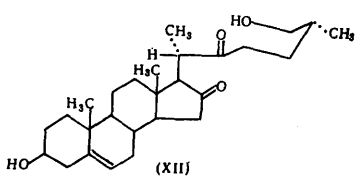


(X)



(XI)

The structure and stereochemical configuration of solasodine were confirmed by its synthesis from cryptogenin (XII):[4]

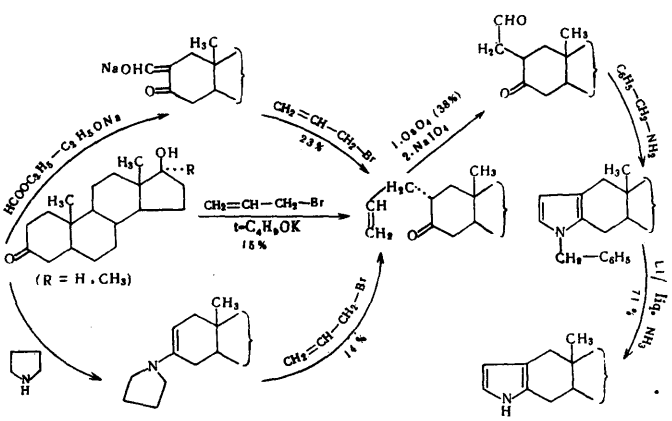


(XIII)

The scope of the present review does not permit dwelling in detail on the chemistry of the steroidal sapogenins and alkaloids, particularly as the problems of the structure and properties of these compounds have received detailed consideration in the literature[3].

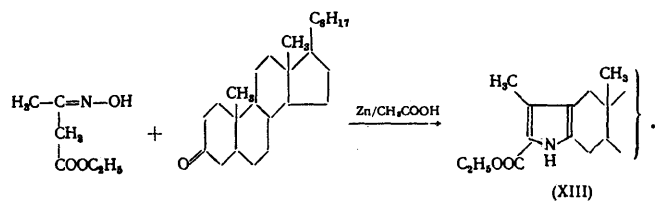
2. Pyrrolo-, Pyrrolidino-, and Indolo-Steroids

The attachment of a pyrrole ring to the steroid skeleton is effected on the basis of a general method of cyclising 1,4-dicarbonyl compounds by heating them with ammonia or primary amines at 100°. The necessary 1,4-dicarbonyl derivatives of the steroids are obtained by the following scheme[5]:



When an acetoxy-group is present at $C_{(17)}$, the debenzylation in the last stage is accompanied by deacetylation. During the direct allylation of the initial ketone with allyl bromide and potassium t-butoxide, the 4α-allyl derivative is also formed as a side-product, but it could not be converted into the corresponding pyrrole[5].

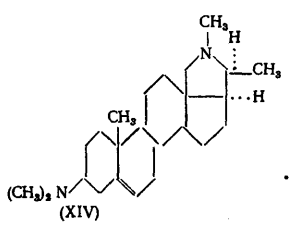
The Knorr method was also used successfully for obtaining pyrrole derivatives of steroids. By using it in the condensation of cholestan-3-one with the oxime of acetoacetic ester, ethyl 5′-carboxy-4′-methylcholestano[3,2-*d*]-pyrrole (XIII) was obtained[6]:



(XIII)

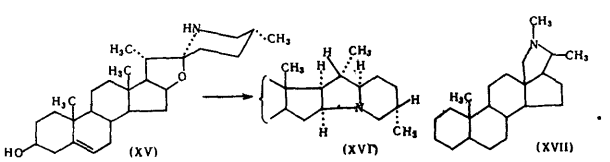
Androst-4-en-3,17-dione was converted analogously into the ethyl ester of 3′-carboxy-2′-methylandrosta-4,16-dien-17-ono[3,2-*d*]pyrrole[6]. However, cholest-4-en-3-one could not be converted into the corresponding pyrrole derivative.

Pyrrolidine derivatives of steroids are also known, mainly among the steroid alkaloids isolated from plant materials. For example, the most widely distributed and most important representative of the alkaloids isolated from the seeds of various species of the Indian shrub *Holarrhena* is conessine (XIV) which was recently synthesised, starting from derivatives of 5α-pregnane or pregn-5-ene[7,8]:



(XIV)

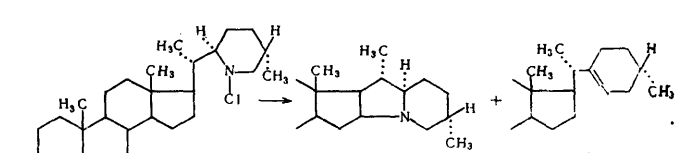
Δ⁵-Tomatidine (XV) formed the basis of a recent synthesis of the steroidal alkaloid solanidine (XVI) which contains a condensed perhydropyrrocoline ring[9]:



(XV) (XVI) (XVII)

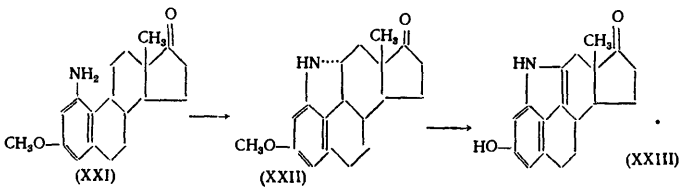
As a result of extensive investigations carried out by a large group of French investigators[10-12] it was found that various species of *Apocynaceae* are also rich in steroid alkaloids which are derivatives of conamine (XVII). The latter contains a pyrrolidine ring but pregnane is always the basis of the skeleton and therefore these alkaloids can be used for the industrial production of various pregnane derivatives[13].

An interesting observation was made during the treatment of *N*-chlorosteroidamines with 5% KOH in methanol: in this the chloroamine (XVIII) gives 57% of the alkaloid demissidine (XIX) and 3.5% of the azomethine (XX); on the other hand the (22 *S*, 25 *R*) isomer (XIX) under these conditions does not form demissidine and is converted into the azomethine in 60% yield[14]:



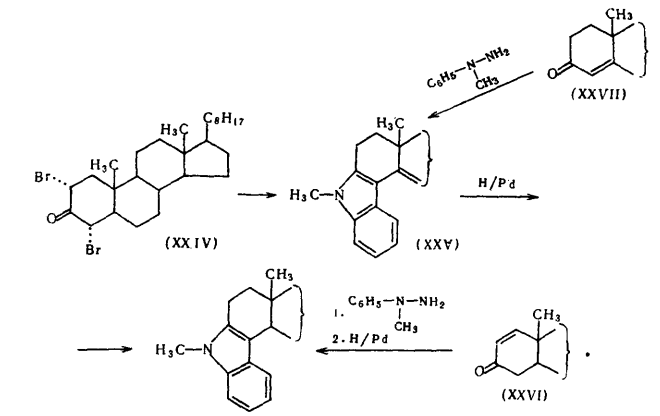
(XVIII) (XIX) (XX)

Quite recently the synthesis of a new, interesting steroid heterocyclic system was proposed[15]. It appeared that on diazotisation of 1-amino-3-methoxyoestra-1,3,5(10)-trien--17-one (XXI) and subsequent treatment with sodium azide, the 1-azido-derivative is obtained, which on heating in n-hexadecane is converted into indoline (XXII). This, by a series of conventional transformations is converted with high yield into the final product, 3-hydroxy-1,11-imino--oestra-1,3,5(10),9(11)-tetraen-17-one (XXIII):



(XXI) (XXII) (XXIII)

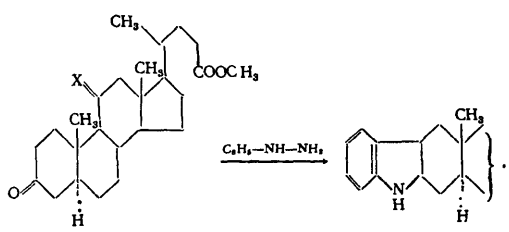
In 1937, during the dehydrobromination of 2α,4α-dibromocholestan-3-one (XXIV) with dimethylaniline a compound was obtained[16] which on the basis of subsequent investigations[17] was given the structure (XXV). The structure proposed was confirmed by counter-synthesis from cholest-1-en-3-one (XXVI) and cholest-4-en-3-one (XXVII) and α-methylphenylhydrazine by the Fischer reaction, and also by infrared and ultraviolet spectroscopy[17].



(XXVII) (XXIV) (XXV) (XXVI)

More detailed proof of the structure (XXV) of the compounds obtained has been given recently[18].

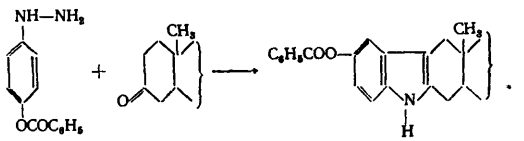
The Fischer reaction has also been employed successfully for obtaining other indole derivatives of the steroids. Thus in the reaction of methyl 3-ketocholanate (XXVIII; X = H_2) and its 12-keto-derivative (XXVIII; X = O) with phenylhydrazine in acetic acid the indole derivative (XXIX) was obtained, condensed with the steroid nucleus in positions 2 and 3 of the pyrrole ring[6]:



(XXVIII) (XXIX)

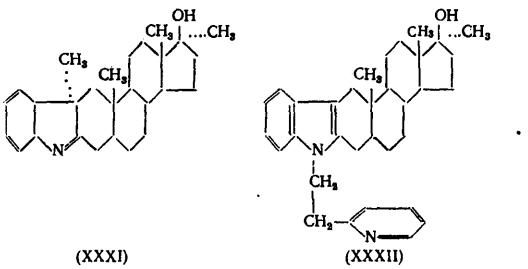
where X = H, O.

In the search for steroid analogues of 5-hydroxytryptamine and with the aim of investigating them as hypotensive agents, a group of English investigators recently developed a synthesis of androstano[2,3-*b*]-5′-hydroxyindole derivatives from 3-keto-steroids and *p*-benzoyloxyphenylhydrazine (XXX) by the following scheme[19]:



(XXX)

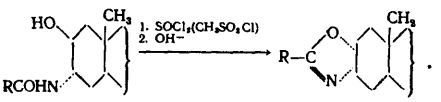
On starting from 17β-hydroxy-2α,17α-dimethylandrostan-3-one and phenylhydrazine, the indolenine (XXXI) was obtained, and the reaction of androstanoindoles with 2-vinylpyridine in dimethylformamide in the presence of sodium gave compounds of the type of (XXXII). Replacing the vinylpyridine by 2-methyl-5-vinylpyridine did not lead to a positive result[19]:



(XXXI) (XXXII)

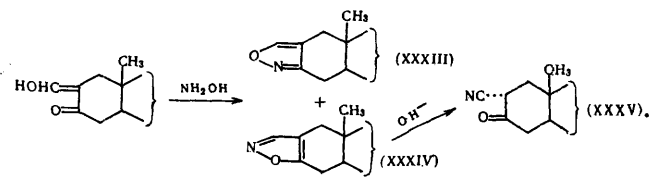
3. Oxazolino-, Isoxazolo-, and Isoxazolino-Steroids

On treating the acyl derivatives of *trans*-amino-alcohols with thionyl chloride or methanesulphonyl chloride and then washing with alkali, various 2′-substituted oxazolinosteroids were obtained[20,21]. For example, 2β-benzoylamino-3α--hydroxycholestane gives cholestano[3β,2β-*d*]-2′-phenyloxazoline, and 2β-hydroxy-3α-benzoylaminocholestane gives cholestano[3α,2α-*d*]-2′-phenyloxazoline[21]:



Owing to their considerable biological activity the methods of synthesis and properties of isoxazole derivatives of steroids have been studied in considerable detail.

Even in 1925 it was shown[22] that in the reaction of hydroxymethylenecyclohexanone with hydroxylamine a mixture of isomeric [2,3-*d*]- and [3,2-*c*]-isoxazoles is formed. The same method is successfully used for the synthesis of steroidoisoxazoles[23]. Usually for this purpose the hydroxymethyleneketosteroid is boiled with hydroxylammonium chloride in alcohol in the presence of sodium acetate. As in the condensation of hydroxymethylenecyclohexanone, the steroid hydroxymethyleneketones also form two isomers (XXXIII) and (XXXIV):[23]



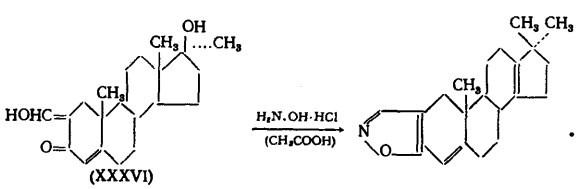
(XXXIII) (XXXIV) (XXXV).

To separate them use is made of the ability of the [2,3-*d*]isoxazoles (XXXIV) to be readily converted into α-cyanoketones (XXXV) on treatment of the reaction mixture with alkali[24]. For example[25], in the reaction of 2-hydroxymethylene-17α--methyldihydrotestosterone with hydroxylamine the reaction product is treated with sodium methoxide, whereupon the [2,3-*d*]-isomer is quantitatively converted into 1-cyano--17α-methyldihydrotestosterone, but the [3,2-*c*]-isomer (XXXIII) is recovered unchanged from the reaction medium in 41% yield calculated on the initial hydroxymethylene-ketone. 2α-Cyanocholestan-3-one could only be made by this means[26]. Hence this process was also shown to be a convenient preparative method for the introduction of the cyano-group into the $C_{(2)}$ of the steroid nucleus, which could not be achieved by a direct path.

It was shown that the rate of formation of (XXXIII) and (XXXIV) is greatly dependent on the pH of the medium, the solvent, and the temperature[27]. This fact is of great importance for the development of a process for the synthesis of [2,3-*d*]isoxazolosteroids, which are of greater interest as regards their biological activity than their [3,2-*c*]-analogues. In a weakly alkaline medium a mixture of isoxazoles is usually formed[28]. Unsaturated steroid hydroxymethyleneketones with a Δ^4 double bond are converted under these conditions only into [2,3-*d*]isoxazoles[25]. The same products are also formed in the presence of a 4,4-*gem*-dimethyl group in the molecule of the initial hydroxymethyleneketone[28].

On carrying out the reaction in glacial acetic acid one isomer (XXXIV) is also formed preferentially.

It should be noted that when a secondary hydroxyl is present at $C_{(17)}$ in the molecule of the initial steroid, on carrying out the reaction in acetic acid its acetylation also occurs[28]. When a hydroxymethyleneketone containing a tertiary hydroxyl at $C_{(17)}$ is introduced into the reaction, dehydration with a Wagner–Meerwein rearrangement takes place, as, for example, with 2-hydroxymethylene-17α--methyltestosterone (XXXVI).[29] This behaviour can be avoided if the reaction is carried out in weakly acid medium with the addition of an excess of sodium acetate[28]:



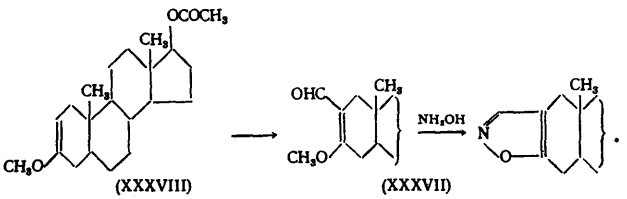
(XXXVI)

The structure of the products of the rearrangement is shown[29] by the absence of hydroxyl absorption and splitting of the band at 1380 cm^{-1} in the infrared spectrum and by the presence of a singlet in the NMR spectrum at 9.03 τ, the intensity of which corresponds to the nine protons of the three methyl groups[29].

The methyl group which had migrated is ascribed the β-configuration, since it is known[30] that the Wagner–Meerwein rearrangement proceeds without change of configuration.

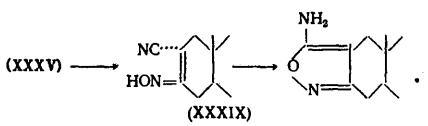
Cortisone is converted analogously into 2-hydroxymethylenecortisone, which on treatment with hydroxylamine forms 17α,21-dihydroxypregn-4-en-11,20-diono[2,3-*d*]-isoxazole[25].

The acetate of 2-formyl-3-methoxyandrost-2-en-17β-ol (XXXVII) — obtained by the formylation of the acetate of 3-methoxyandrost-2-en-17β-ol (XXXVIII) by the Vilsmeier reagent — was recently used for the preparation of [2,3-*d*]isoxazoles[31]:



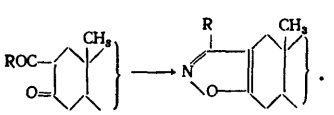
(XXXVIII) (XXXVII)

It is interesting to note that the 2α-cyanoketones which are obtainable on the basis of [2,3-*d*]isoxazoles can be used for the synthesis of steroido[3,2-*c*]-5′-aminoisoxazoles (XXXIX).[32] Condensation of these compounds is carried out either with hydroxylammonium chloride in a pyridine solution, or with hydroxylammonium acetate in ethanol. The reaction proceeds with the intermediate formation of an oxime:



(XXXIX)

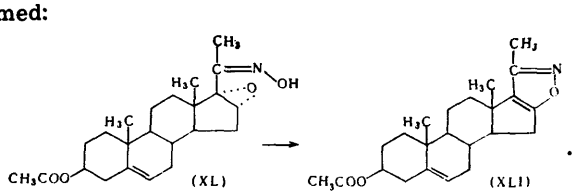
Isoxazolosteroids were also synthesised on the basis of corresponding β-diketones. In the condensation of 2-aryl--3-ketosteroids with hydroxylamine [2,3-*d*]isoxazoles are obtained which contain alkyl substituents in position 3 of the isoxazole ring[33]:



where R = CH_3, n-C_3H_7.

To retain the keto-group, it is first either blocked or reduced and the resulting hydroxyisoxazole oxidised with chromium(VI) oxide in pyridine[29].

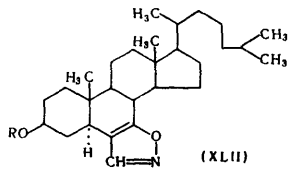
A series of steroidoisoxazoles of a new type was recently obtained[34]. When the oxime of the acetate of 16α,17α-epoxy-3β-hydroxypregn-5-en-20-one (XL) is treated with phosphoryl chloride in pyridine the acetate of androst-5-en-3β-ol[17,16-*d*]-3′-methylisoxazole (XLI) is formed:



The product obtained is saponified with alkali into an alcohol, which in turn is smoothly oxidised after Oppenauer to the 3-keto-derivative.

For the identification of the steroidoisoxazoles, use can be made of the fact that the ultraviolet spectra of all the isoxazoles which do not contain a Δ^4 double bond have a band at 227 nm but in the presence of a Δ^4 bond there are bands at 207, 209, and 286 nm.[29] For isoxazoles of the

type (XLII) obtained on the basis of 6-hydroxymethylene--7-ketosteroids, an absorption band appears at 231 nm in the ultraviolet spectrum[29]. In general it can be noted that [2,3-*d*]isoxazoles absorb in the ultraviolet region at greater wavelengths than their [3,2-*c*]-analogues, that is, at 227 ± ± 2 and 222 ± 1 nm respectively[28]:

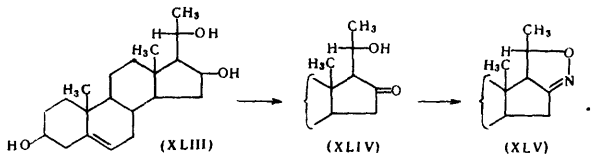


(XLII)

Attachment of the isoxazoline ring to steroids can also be brought about by condensation of hydroxylamine with steroid ketones of suitable structure.

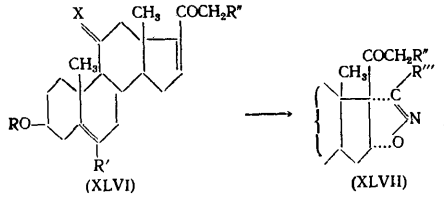
On the basis of 16β,20α-diols (XLIII) selective oxidation gives the corresponding 20α-hydroxy-16-ketosteroids (XLIV), the 16-oximes of which are converted under Beckmann rearrangement conditions (on treatment with tosyl chloride or acetic anhydride in pyridine) into steroido-[16,17-*c*]isoxazolines (XLV) in good yield[35]. The acetate of 3-β-hydroxy-5'-methyl-5α-androstano[16,17-*c*]isoxazoline, a series of Δ⁵-steroido[16,17-*c*]isoxazolines, and also a series of 3-ketoisoxazolines were obtained in this way[35].

Cyclisation proceeds with retention of the configuration at $C_{(20)}$ and the hydrogen atoms at $C_{(17)}$ and $C_{(20)}$ have the *trans* configuration. Evidently, the initial oxime reacts in the *anti*-form; in the opposite behaviour the configuration at the $C_{(20)}$ atom would be the reverse[35]:



(XLIII) (XLIV) (XLV)

The second method of synthesis of steroidoisoxazolines consists in the reaction of αβ-unsaturated ketosteroids with the acid chlorides of hydroxamic acids. This reaction has been well studied earlier in the aliphatic series[36]. To carry out the reaction a catalytic amount of triethylamine is added to a mixture of benzhydroxamic acid chloride and a derivative of 16-dehydro-pregn-5-en-20-one (XLVI) in tetrahydrofuran at 0°. The corresponding steroido[17,16-*d*]--3'-phenylisoxazolines (XLVII; R = C_6H_5) are separated from the reaction medium in ~ 80–90% yield[37]:



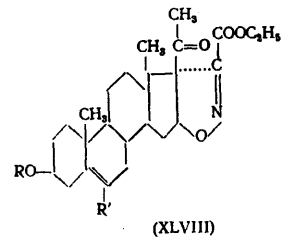
(XLVI) (XLVII)

where R = H, CH_3CO; R' = H, CH_3; R'' = H, OH; R''' = = CH_3, C_6H_5; X = H_2, O.

Saponification of the 3-acetyl derivatives (XLVII; R = = CH_3CO) to the corresponding alcohols and oxidation of the latter after Oppenauer can be used to obtain 3-ketosteroido-isoxazolines[37].

3'-Methylisoxazolines (XLVII; R''' = CH_3) were obtained by the above scheme with a yield of ~ 69–99.8% in the presence of an excess of acethydroxamic acid[37].

The reaction of natural 16-dehydro-20-ketopregnane derivatives with ethyl oxalate nitrile oxide gives isoxazolines of type (XLVIII):[38]



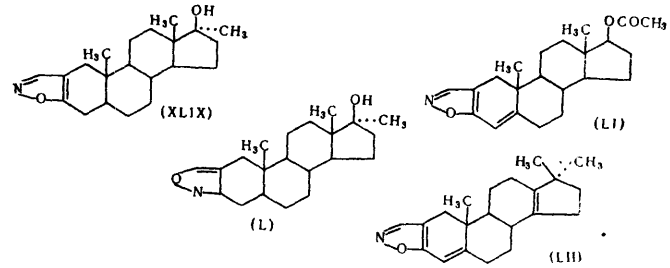
(XLVIII)

where R = H, CH_3CO; R' = H, CH_3.

In the ultraviolet spectrum of all the isoxazolines synthesised the chromophoric group $-N=C-C_6H_5$ appears by three absorption bands at 212, 218, and 262 nm.[37]

The steroidoisoxazoles are a new class of modified steroid hormones which exhibit an interesting physiological activity. It was shown by analogy with steroidopyrazoles that the attachment of an isoxazole ring also brings about interesting changes in the activity of the initial steroids. The most interesting preparation of this class was 17α-methylandrostan-17β-olo[2,3-*d*]isoxazole (XLIX), which in comparison with methyltestosterone exhibits 9.7 times more anabolic, twice the miotropic, and 0.24 times the androgenic activity[28].

Almost the same activity is exhibited by androstan-17β--olo[2,3-*d*]isoxazole[28]. Contrary to the corresponding pyrazoles these compounds are completely devoid of oestrogenic activity[23]. 17α-Methylandrostan-17β-olo[3,2-*c*]-isoxazole (L) was a strong anabolic agent. Two preparations (LI) and LII) were effective anti-tumour agents[30]:



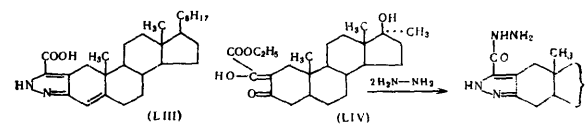
(XLIX) (LI) (L) (LII)

The introduction of additional 4,4-dimethyl- or 6α-methyl--3'-alkyl substituents lead to minimal myotropic activity[28].

The 19-nor derivatives have the least interest. The completely saturated products always have greater activity than their Δ⁴- and Δ⁴,⁶-analogues[28].

4. Pyrazolo- and Pyrazolino-Steroids

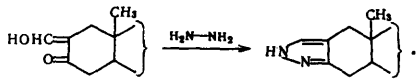
The first steroid pyrazole was 5'-carboxycholest-4--eno[3,2-*c*]pyrazole (LIII), obtained by condensation of 2-oxalylcholestenone with hydrazine[39]. Afterwards certain transformations were performed on 2-oxalyl-17α-methyldihydrotestosterone, which can be obtained from ethyl oxalate, sodium methoxide, and the corresponding 3-keto--steroid[32]:



(LIII) (LIV)

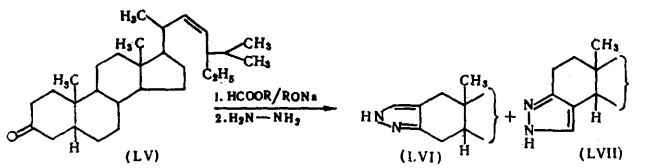
It was shown[40] that steroido[3,2-*c*]pyrazoles form a new class of steroid hormones with interesting physiological activity.

The main method of synthesis of the compounds of this class is the condensation of steroidohydroxymethyleneketones with an excess of hydrazine:



Hydroxymethyleneketones are readily obtained by formylation of the corresponding ketones with ethyl formate in the presence of sodium hydride or ethoxide in benzene or dioxan solution of either saturated or unsaturated ketones[41].

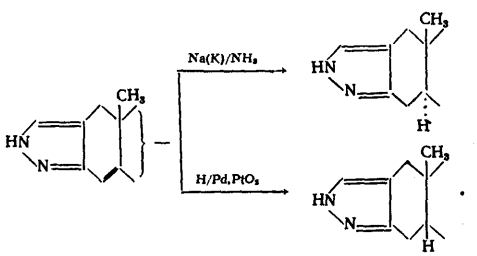
Note that both for A/B-*trans*- and for A/B-*cis*-3-ketosteroids only the 2-formyl derivatives are obtained in good yields (~ 70–90%); these are considerably more stable thermodynamically than the corresponding 4-formyl derivatives[42]. The only exception is 5β-stigmast-22-en-3-one (LV), which on formylation gives a mixture of the 2- and 4-formyl-5β-stigmast-22-en-3-ones, and under the action of hydrazine these are converted into pyrazole derivatives (LVI) and (LVII), readily separable chromatographically[42]:



Partial formylation at $C_{(4)}$ is here the result of the formation of an intermediate derivative with a very low solubility which immediately upon formation undergoes further reversible conversion into the 2-hydroxymethyleneketone[43].

Hence formylation of 3-keto-steroids with subsequent condensation with hydrazine readily gives the corresponding A/B-*trans*- and A/B-*cis*-steroido[3,2-*c*]pyrazoles[43].

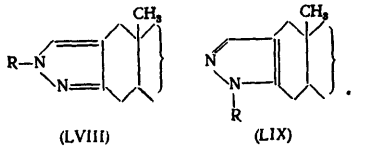
Another path for the production of 5α- and 5β-steroidopyrazoles consists in the selective reduction of readily accessible Δ^4-steroidopyrazoles. It has been shown that in the catalytic hydrogenation over palladium or platinum(IV) oxide the 5β-isomers are obtained[42,43], but in reduction with alkali metals in a mixture of liquid ammonia, tetrahydrofuran, and ethanol only the 5α-isomers are obtained, with yields of 62–76%:[44]



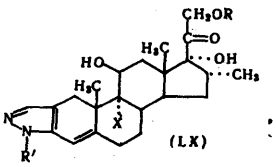
Reduction of the aromatic pyrazole ring during the hydrogenation is not observed[44].

It would be expected that condensation of 2-hydroxymethylene-3-ketosteroids with substituted hydrazines should give, depending on the reaction conditions, mixtures of 1′- and 2′-substituted pyrazoles (LVIII) and (LIX).[45]

However, as was shown for an alkylhydrazine, the substituted nitrogen of which has a more nucleophilic character, only the isomer (LVIII) is obtained, and for phenylhydrazine, in which the β nitrogen atom is more nucleophilic, isomer (LIX) is obtained[46]:

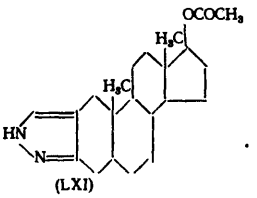


Extensive studies of the steroidopyrazoles were made by Hirschmann and coworkers[47-50]. They synthesised certain 5α-pregn-4-eno[3,2-*c*]pyrazoles (LX) based on cortisol and its 16α-methyl and dihydro-derivatives through their hydroxymethylene derivatives,

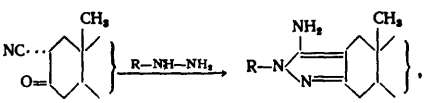


where R = H, CH_3CO; R′ = H, C_6H_5, p-FC_6H_4; X = H, F.

It was recently shown[31] that on treating the acetate (XXXVIII) with hydrazine the corresponding 5α-pyrazole (LXI) is formed:

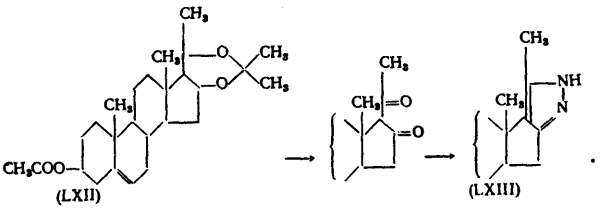


A series of 5′-amino-substituted steroidopyrazoles was obtained by condensation of 2α-cyano-3-ketosteroids with hydrazine[32]:



where R = H, CH_3.

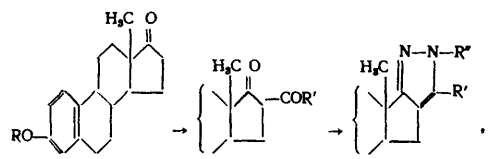
The 16β,20α-isopropylidenehydroxysteroids of type (LXII) are also of interest for the synthesis of the steroidopyrazoles. These are readily converted into 16,20-diketones, which form with hydrazine in ethanol pyrazole derivatives (LXIII), in which the heterocyclic ring is condensed with a steroid component in positions 16 and 17:[51]



Analogous results were also obtained on the basis of 5α-pregnan-3β,16β,20α-triol.[52]

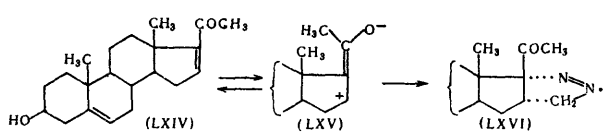
It should be noted that in the Wolff–Kishner reduction of 16α,17-epoxyhydroxypregnenone, in addition to a mixture of difficultly separable diols androst-5-en-3β-olo[16,17-*c*]--5′-methylpyrazole is formed[53].

According to the results of Italian chemists[54], the synthesis of [17,16-*c*]pyrazoles of the androstane and oestrane series is conveniently effected by treatment of 17-ketosteroids with ethyl formate or diethyl oxalate in the presence of sodium hydride or methoxide with subsequent cyclisation with hydrazines of the 16-formyl derivatives obtained:

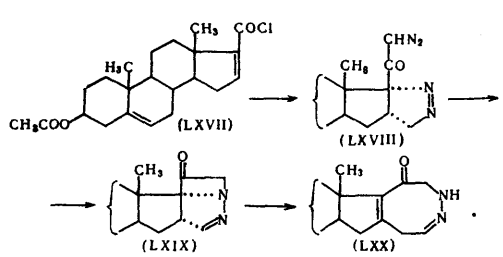


where R = H, CH_3,  ; R′ = H, $CO_2C_2H_5$; R″ = H, CH_3.

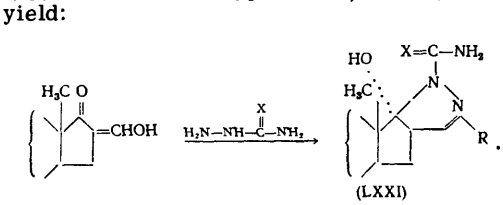
It is known that αβ-unsaturated ketones, esters of carboxylic acids, and nitriles add on diazoalkanes to form pyrazolines. This reaction also proved possible in the steroid series. In the reaction of diazomethane with 16-dehydro--20-ketopregn-5-en-3-ol (LXIV) or (LXV), 20-ketopregn--5-en-3-olo[17,16*c*]pyrazoline (LXVI) is formed[55]:



When the acid chloride (LXVII) is reacted with diazomethane, a 21-diazopyrazoline (LXVIII) is formed, evidently as a result of the addition of diazomethane to the unsaturated diazomethyl ketone. The (LXVIII) thus obtained gives with warm acetic acid the compound 3β-acetoxy-16α,17α,21--[3,1,1-(2-pyrazolino)]pregn-5-en-20-one (LXIX).[56,57] When (LXIX) is heated on the steam-bath in acetic acid with a large quantity of sodium acetate, the diazepinone (LXX) is formed in 16% yield. The derivative obtained is successfully methylated and acetylated on nitrogen, but does not form an oxime or semicarbazone at the carbonyl group[56,57]:



When semicarbazide, thiosemicarbazide, and some of its derivatives react with 16-hydroxymethylene-17-ketosteroids, pyrazolines of the type (LXXI; R = H) are formed in high yield:



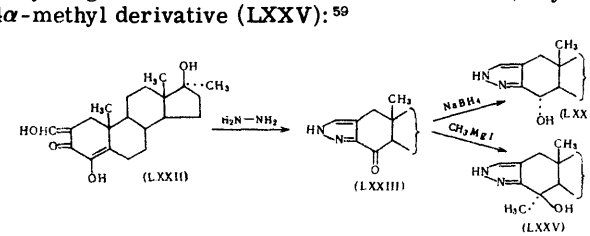
With 16-ethoxyallyl-17-ketones, the pyrazolines (LXXI; R = $CO_2C_2H_5$) are formed[58].

On heating in a bomb with methyl iodide, 1′-methylsteroido[3,2-*c*]pyrazoles are converted into 1′,2′-dimethylpyrazolium salts, which are stable, high-melting compounds, relatively poorly soluble in water[46].

On treating the steroidopyrazoles with acid anhydrides, *N*-acyl derivatives are obtained, which, however, readily lose an acyl group on boiling in aqueous acetic acid. In an attempt to methylate the unsubstituted nitrogen of *N*-acyl pyrazoles the *N*-acyl group is detached and 1′,2′-dimethylpyrazolium salts are formed[46].

Treatment of steroido[3,2-*c*]pyrazoles with potassium cyanate in dilute alcoholic solution with hydrogen chloride leads to the corresponding *N*-carbamoyl derivative[46]. These compounds, like the *N*-acylpyrazoles, are of interest for the temporary protection of the NH group of the pyrazole ring, since the carbamoyl group can also be readily removed on boiling with an excess of hydrogen chloride in aqueous alcohol.

In the presence of a secondary hydroxyl group at $C_{(17)}$ of the steroid pyrazoles it can be oxidised by a mixture of sulphuric and chromic acids in dimethylformamide to the 17-keto-group[46]. To obtain 4-ketoandrostane derivatives, a start is made from 4-hydroxy-2-hydroxymethylene-17α--methyltestosterone (LXXII), which is condensed with hydrazine in ethanol, forming the compound (LXXIII).[59] With the aid of sodium tetrahydroborate, the pyrazole (LXXIII) is reduced to the 4-hydroxy-derivative (LXXIV) and with methylmagnesium iodide is converted into the 4β-hydroxy--4α-methyl derivative (LXXV):[59]



All the androstano[3,2-*c*]pyrazoles have a characteristic absorption maximum in their ultraviolet spectrum at 223 nm (ε ~ 5000), which is displaced in 0.01 *N* alcoholic hydrogen chloride solution to 229 nm (ε ~ 6200). When a conjugated double bond is present the steroidopyrazoles have absorption maxima in the 261 nm region (ε ~ 10 000). The bathochromic shift of the maxima in the acid solution is explained by the protonation of the pyrazole ring, since such a phenomenon is not observed in alcoholic alkali solution[46].

The fusion of a coplanar pyrazole ring to the steroid nucleus leads to substitution of the $C_{(3)}$ oxygen atom by nitrogen which changes the nucleophilic environment in this region. In this there is a change in the distance between the active centres of the steroid molecule at $C_{(3)}$ and $C_{(17)}$, since the length of the C=N bond is ~ 1.4 Å, and the length of the C=O bond in the original ketone is 1.2 Å. This evidently shows some influence of the strength of the bond of the steroid molecule with the chelate receptors and can lead to selectivity in the reaction between the steroid and the receptor[46].

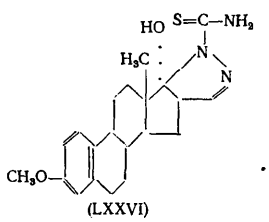
It would also be expected that in this there would be a significant fall in the oestrogenic activity[60], which is in fact observed[46].

The androgenic and anabolic activity drops sharply on the introduction at $C_{(17)}$ of alkyl residues greater in volume

than ethyl and also during *N*-methylation. However, the acylation of the pyrazole nucleus does not alter the activity, probably owing to the lability of the *N*-acyl groups. Activity of the same order is observed in Δ^4- and $\Delta^{4,6}$-steroido[3,2-*c*]-pyrazoles [46].

The introduction of substituents into the steroid nucleus has the most influence on the activity of steroidopyrazoles. But whereas the activity of 9α-fluoro-11β-hydroxy-6α--methyl derivatives of 17α-methyltestosteroid is higher than that of 17α-methyltestosteroid itself, the introduction of analogous substituents into the steroido[3,2-*c*]pyrazole molecule appreciably reduces its activity [46]. The activity of 4-methyl- and 19-nor-steroidopyrazoles is greatly diminished and the 4-keto-, 4-hydroxy-, and 4α-methyl--pyrazoles are completely inactive (LXXIII)–(LXXV). [59] The physiological activity mentioned is completely absent from compounds with the pyrazole ring in positions 16 and 17. [54]

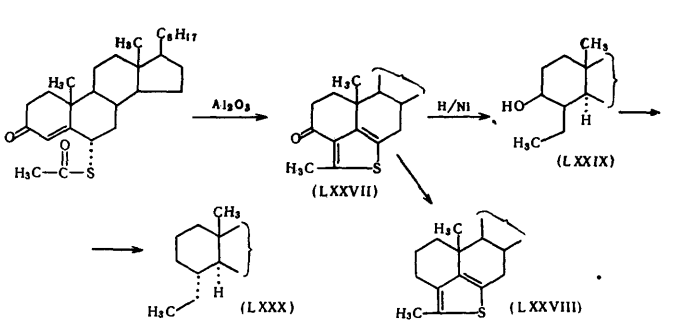
The pyrazoline (LXXVI) is an effective hypocholesterinemic agent at very low oestrogenic activity [58], but some pyrazoles of type (LX) were very interesting in their anti--inflammatory activity [49]. The authors assumed that these pyrazoles are active as such and not as a result of biological release of the 3-keto-group:



(LXXVI)

5. Thienosteroids

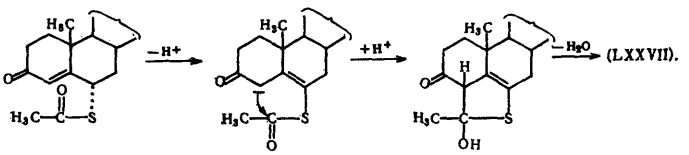
The first representative of the class of thienosteroids was obtained in 1963 [sic] from 6α-thioacetylcholest-4-en--3-one. [61] During the chromatography of this product on an aluminium oxide column the authors unexpectedly observed that cyclisation occurs with the formation of a thiophene derivative, which on the basis of chemical properties and the ultraviolet and infrared spectra was ascribed the structure (LXXVII). [62] This compound was converted, by a Huan-Minlon reduction, into a thiophen derivative of cholestane (LXXVIII). Catalytic reduction of (LXXVII) over Raney nickel leads to the formation of 4β-ethylcholestan-3β-ol (LXXIX), from which 4α-ethylcholestane (LXXX) is obtained by known methods [62]:



(LXXVII) (LXXIX) (LXXX) (LXXVIII)

The intramolecular condensation described has also been used with progesterone, testosterone, and their derivatives [62]. Always, derivatives were obtained analogous in structure to the cholestanone derivative (LXXVII).

Probably the reaction includes enolisation of a Δ^4-3-ketone with later formation of an anion at $C_{(4)}$ by the following scheme [62]:



(LXXVII).

Use of different catalysts of a basic character confirms the suggested mechanism. Treatment of 6α-acetylthio-19-nor-testosterone acetate with potassium t-butoxide and trimethylmethanol gives the corresponding 17-hydroxythieno--derivative in 39.5% yield, but on boiling with sodium hydride in toluene the yield of product is increased to 56.6%. [63]

Thienosteroids can be identified by the presence of characteristic absorption bands in the ultraviolet spectrum (220, 268, and 304 nm). [63]

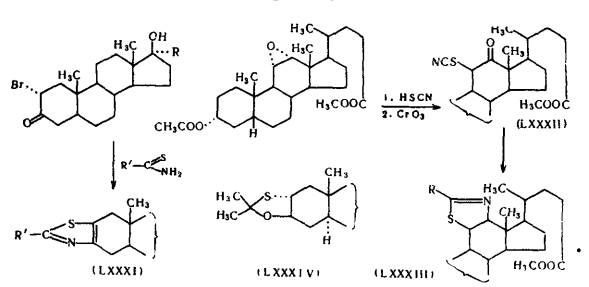
6. Thiazolosteroids

Although methods of synthesising thiazoles have been studied rather thoroughly [64], the addition of this heterocycle to compounds of the steroid series was only accomplished in 1960. [25] Thiazolosteroids were obtained by condensing 2α-bromodihydrotestosterone with thioformamide or thioacetamide in alcoholic solution with the formation of products of structure (LXXXI). [25,65]

In developing this, Doorenbos and Dorn [66] made a detailed investigation of the condensation of 2α-bromo-17α-methyldihydrotestosterone with acid thioamides, thiourea, phenyl- and allyl-thiourea, and thus obtained thiazole derivatives of the general formula (LXXXI).

The addition of the thiazole ring in positions 11 and 12 to acetylmethyl cholanate was achieved by Japanese investigators [67]. These syntheses started from the 11α,12α- and 11β,12β-epoxysteroids, which under the action of thiocyanic acid in ether easily form thiocyanato-compounds. Chromium(VI) oxide in acetic acid oxidises the latter into 12-keto-11β-thiocyanato-compounds (LXXXII). On boiling these compounds with secondary amines in dioxan solution, closing of the thiazole ring takes place with the formation of substituted derivatives of cholano[12,11-*a*]thiazole (LXXXIII).

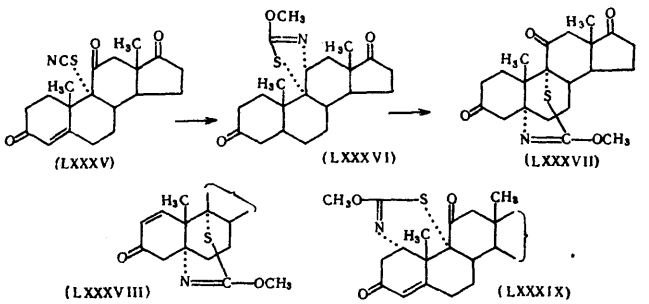
It was also shown [68] that on heating 2α-thiocyanatocholestan-3-one in dioxan containing hydrochloric acid, an oxothioline is formed in good yield (LXXXIV).



(LXXXI) (LXXXIV) (LXXXIII)

On treating 9α-thiocyanatoandrost-4-en-3,11,17-trione (LXXXV) with a water–methanol solution of potassium

carbonate at ordinary temperature 2′-methoxyandrost-4--eno-3,17-diono[11α,9α-*d*]thiazoline (LXXXVI) is formed in good yield[69]. When the thiazolines thus obtained are boiled or kept for a long time in methanol solution, rupture of the $C_{(11)}$–N bond takes place with formation instead of a $C_{(5)}$–N bond, such as, for example, the conversion of (LXXXVI) into (LXXXVII).[70] The necessary condition for such a type of isomerism is the presence of an αβ-unsaturated keto-system. 1,4-Dienones are also isomerised but considerably more slowly, and this results in the formation of a mixture of (LXXXVIII) and (LXXXIX):

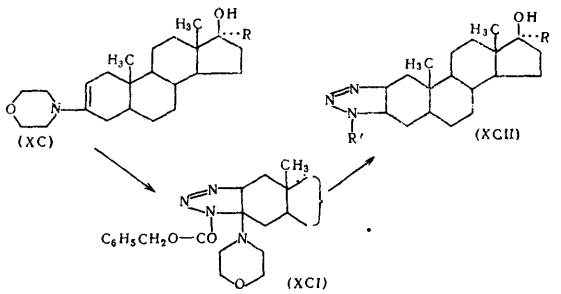


According to the results of biological tests[65], 2′-methyl 17α-hydroxy-17β-methylandrostano[3,2-*d*]thiazole is a strong anabolic agent.

7. Triazolosteroids

The methods of adding a triazole ring to a steroid system have been inadequately studied. Only one method of synthesising compounds of this type has been investigated[71], based on the condensation of enamines[72] of steroid ketones with various azides. In this way, from 3-morpholylenamines of dihydrotestosterone and its 17α-methyl derivative (XC) the corresponding *N*′-carbobenzoxy-3-(*N*-morpholyl)-5α--androstan-17β-olo[2,3-*d*]triazoles (XCI) were obtained. In removing the morpholine ring by reduction with palladium on carbon or lithium tetrahydroaluminate, androstano-[2,3-*d*]triazoles (XCII; R′ = H) were obtained.

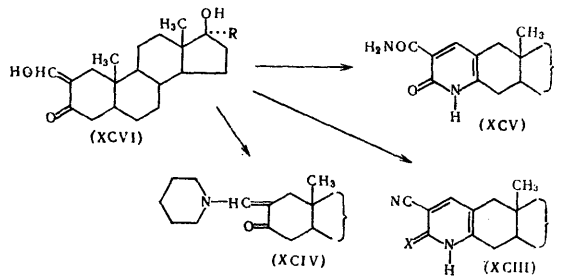
By reaction of dihydrotestosterone with phenyl azide, *N*′-phenyl-5α-androst-2-en-17β-olo[2,3-*d*]triazole (XCII; R = H; R′ = C_6H_5) is obtained, and from the 17α-methyl derivative (XC) the corresponding 17α-methyltriazole (XCII; R = CH_3, R′ = C_6H_5).



III. STEROIDS CONDENSED WITH SIX-MEMBERED HETEROCYCLES

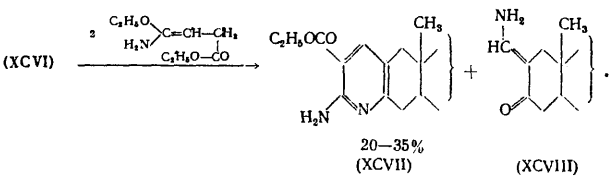
1. Pyridino- and Quinolino-Steroids

On boiling an ethanol solution of dihydro-2-hydroxymethylenetestosterone and its 17α-methyl derivative with cyanoacetamide in the presence of triethylamine the corresponding 5′-cyanosteroido[3,2-*b*]pyrid-6′-ones (XCIII) are obtained[73]. Triethylamine is necessary for this conversion, because on replacing it by sodium ethoxide reaction does not occur, and in the presence of piperidine only a 2-piperidinomethylene-3-keto-derivative is obtained (XCIV). In the absence of catalyst and solvent at 180° a pyridonocarboxamide derivative (XCV) is formed[73]:

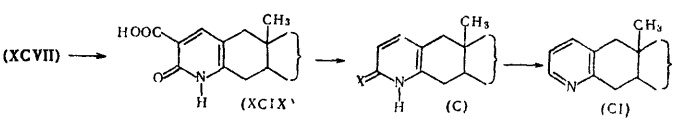


where for (a) X = O, and for (b), X = S; R = H, CH_3.

The condensation of (XCVI) with cyanothioacetamide in methanol proceeds analogously both with triethylamine and with piperidine, with the formation of thiopyridones (XCIIIb) in good yield. This condensation does not occur when a Δ^4 double bond is present, although these same Δ^4 compounds condense well with the amide amidine of malonic acid or with ethyl 3-amino-3-ethoxyacrylate, pyridine derivatives (XCVII) being formed[74]. Considerable amounts of 2-aminomethylene derivatives (XCVIII) are formed as side-products during this:



For proof of the structure, the products (XCVII) were hydrolysed into carboxypyridone-derivatives (XCIX), which at 300° in a vacuum were decarboxylated into pyridones (Ca). With phosphorus pentasulphide the latter is converted into thiopyridones (Cb), which can also be obtained by condensation of (XCVI) with cyanothioacetamide. Finally, unsubstituted pyridines (CI) are obtained by treatment with dimethyl sulphate in water–methanol solution of potassium hydroxide with subsequent desulphurisation over Raney nickel[73]:

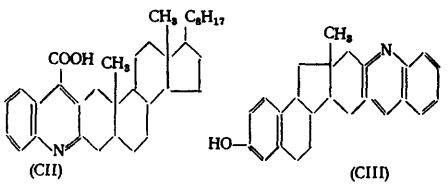


for (a) X = O; for (b) X = S.

In biological tests compounds of the pyridinosteroid class showed a favourable ratio of activity, although to a considerably weaker degree than testosterone propionate[73].

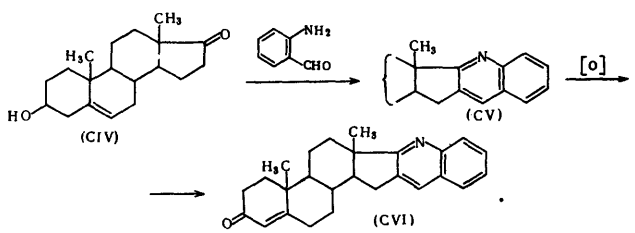
Evidently the first synthetic representative of the quinolinosteroids are the 4′-carboxycholestano[3,2-*b*]quinoline (CII), 4′-carboxyoestrono[17,16-*b*]quinoline (CIII), and the products of their decarboxylation[75], obtained by condensation of the corresponding steroid ketones with isatin by the

Pfitzinger reaction. It was found[75] that the sodium and potassium salts of these acids exhibit strong haemolytic activity:



(CII) (CIII)

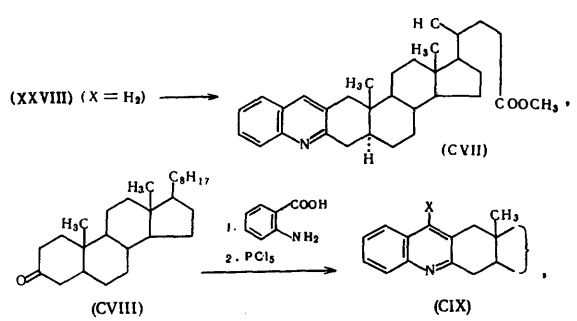
The Friedländer reaction has been used successfully for making steroidoquinolines. For example, condensation of androst-5-en-3β-ol-17-one (CIV) with *o*-aminobenzaldehyde in a basic medium gave androstano[17,16-*b*]quinoline (CV) in 90% yield[76], which is smoothly oxidised after Oppenauer into an αβ-unsaturated ketone (CVI). The quinoline (CV) was also obtained by counter-synthesis from (CIV) by the Pfitzinger reaction[76]:



(CIV) (CV) (CVI)

Analogous conversions were performed in a series of 5,6-dihydro-derivatives of the initial steroids[76].

The methyl ester (CVII) was obtained from the methyl 3-ketocholanate in this way[6]:



(CVIII) (CIX)

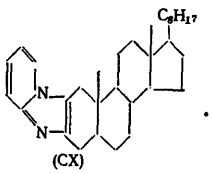
for (CVIII), X = OH; for (CIX), X = Cl.

On heating cholestan-3-one with *o*-aminobenzoic acid, 4′-hydroxyquinoline (CVIII) was synthesised, which on reaction with phosphorus pentachloride or phosphoryl chloride is converted into the 4′-chloro-derivative (CIX).[6]

However, attempts to condense unsaturated ketones (cholestenone, testosterone) with isatin were unsuccessful[75] and also there was no success in obtaining quinolino-[3,4-*b*]steroids from 2,2-dimethylcholestanone even under severe conditions[76].

The absorption of quinolinosteroids in the ultraviolet region is analogous to that for 1,2,3,4-tetrahydroacridine and 2,3-cyclopentanoquinoline. However, for cyclopentanoquinolines of type (CV), as a result of the increased strain of the ring, a feebly hypsochromic shift of the multiplet absorption in the 305–320 nm region is observed[76].

On treatment of 2α-bromo- or 2α-pyridino-3-ketosteroids with hydroxylammonium chloride in pyridine solution steroid compounds of type (CX) are obtained which contain imidazo[1,2-*a*]pyridine rings[77]:

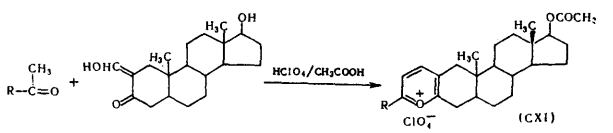


(CX)

2. Derivatives of Steroidopyrylium Salts

In recent years pyrylium salts have attracted the attention of many investigators owing to the high reactivity of the pyrylium cation and the possibility of converting it into various aromatic and heterocyclic compounds[78]. Among the various methods of synthesis of pyrylium salts, that of condensing β-dicarbonyl compounds with methyl and methylene ketones is attractive by its simplicity. Accessible cyclic hydroxymethylene ketones, readily obtainable from cycloalkanes, form pyrylium salts in good yield on condensation with ketones in the presence of perchloric acid[79,80].

It has been shown[81,82] that steroid hydroxymethylene-ketones are also quite convenient starting materials for obtaining steroid compounds with a condensed pyrylium ring:



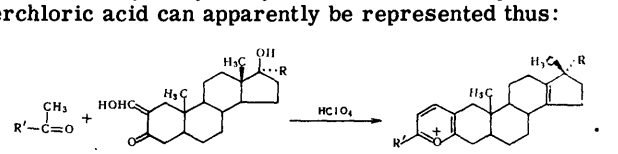
(CXI)

When a mixture of 2-hydroxymethylenedihydrotestosterone with an excess of aliphatic, aliphatic-aromatic, or heterocyclic methyl ketones in glacial acetic acid in the presence of equimolecular amounts of 70% perchloric acid is heated briefly on a water-bath, 6′-substituted 17-acetoxyandrostano[3,2-*b*]pyridylium perchlorates (CXI) are formed[82].

Steroidopyrylium perchlorates exhibit strong fluorescence when irradiated with ultraviolet light and also in solutions.

Under the conditions of the reaction the secondary hydroxyl group of the initial hydroxymethylene ketone is acetylated.

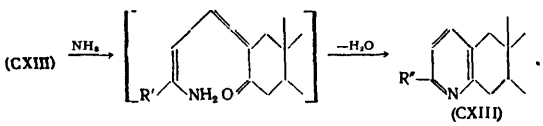
A series of pyrylium derivatives was also obtained on the basis of 2-hydroxymethylene-17α-methyl-[81] and 17α-ethyl--2-hydroxymethylene-dihydrotestosterone[82]. Here, as might be expected, the formation of pyrylium salts is accompanied by loss of the 17β-tertiary hydroxyl with a Wagner–Meerwein rearrangement. Therefore the reaction of the above hydroxymethylene-ketones in the presence of perchloric acid can apparently be represented thus:



(CXII)

The 6′-substituted 17α-alkyl-17β-methylandrost-13--eno[3,2-*b*]pyrylium perchlorates (CXII) which are formed, like other pyrylium salts, react smoothly with ammonia, forming in high yield the corresponding 6′-substituted

steroido[3,2-*b*]pyridines (CXIII). The synthesis of the simplest derivatives of this class by known paths is rather complicated and involves several stages[73] (see p. 33):

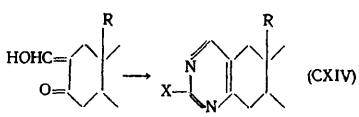


(CXIII)

3. Pyrimidinosteroids

Because many compounds of the pyrimidine series are physiologically active, attempts were made to synthesise condensed pyrimidinosteroids.

Various pyrimidine bases in the steroid series were obtained by the well studied reaction of condensation of 2-hydroxymethylene-5α-androstan-3-ones with guanidine, urea, and thiourea[32]. 2′-Amino-, 2′-hydroxy-, and 2′-mercapto-androstano[3,2-*d*]pyrimidines (CXIV) were obtained in this way. On treating the mercapto-derivative with Raney nickel it is smoothly converted into the unsubstituted derivative (CXIV; X = H):[32]

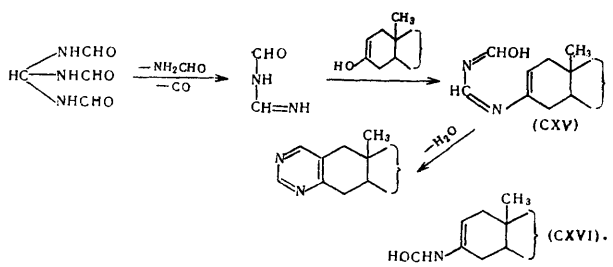


(CXIV)

where R = H, CH_3; X = H, HO, SH, NH_2.

No little interest is also aroused in the synthesis of pyrimidines by the treatment of ketones with trisformylaminomethane in formamide[83]. In this way pyrimidines unsubstituted at C_2' were obtained, identical with the products given by the method described above (CXIV; X = H).

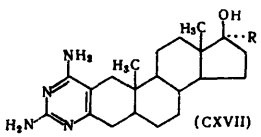
The first stage in the reaction is apparently the formation of a formamidine or formylformamidine which is subsequently cyclised with formation of a pyrimidine derivative by the scheme[84]:



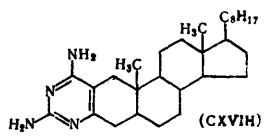
The intermediate compound (CXV) can also be partly decomposed with loss of formamide and formation of a side product (CXVI).

However, the production of pyrimidines in this way is accompanied by low yields. Better results are obtained in the reaction of steroid hydroxymethylene ketones with formamidine or other amidines[25,65,85]. The reaction takes place on prolonged (4–27 h) boiling of an alcoholic solution of a hydroxymethyleneketone, an amidinium chloride, and a base (potassium hydroxide, sodium ethoxide, triethylamine).

Recently a method of synthesising 2′,6′-diaminosteroido-[3,2-*d*]- and 2′,6′-diaminosteroido[17,16-*d*]-pyrimidines[86] was also proposed on the basis of the previously developed condensation of ketones with cyanoguanidine[87]. In this way on the basis of testosterone and its dihydro- and 17α-methyldihydro-derivatives and also cholestan-3-one the corresponding androstano- and cholestano-pyrimidines (CXVII) and (CXVIII) were obtained:



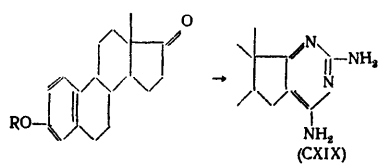
(CXVII)



(CXVIII)

where R = H, CH_3.

Analogous results are also obtained with 17-ketosteroids[86]. Oestrone and its methyl ester are converted into oestra-1,3,5(10)-trien-3-olo[17,16-*d*]-2′,6′-diaminopyrimidines (CXIX):

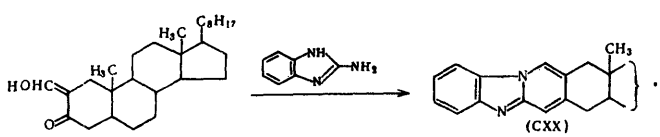


(CXIX)

where R = H, CH_3.

All the diaminopyrimidines obtained exhibit antibacterial activity against certain gram-positive micro-organisms[86], in particular against *Staphylococcus aureus*.

The interesting condensed heterocyclic compound (CXX) was synthesised by condensation of 2-hydroxymethylene-cholestan-3-one with 2-aminobenzimidazole[6]:

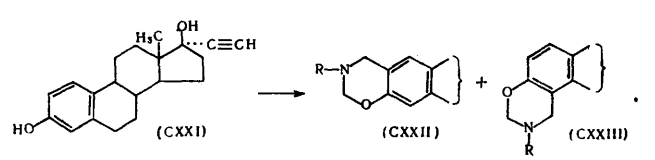


(CXX)

4. Dihydro-Oxazinosteroids

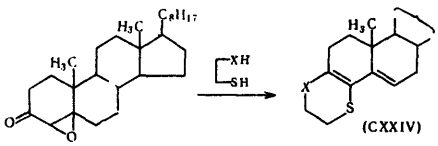
As shown earlier[88], dihydro-*m*-oxazines show specific anti-tumour activity and, unlike other carcinostatic agents, are devoid of toxicity. Because of this, the preparation of dihydro-oxazinosteroids was studied.

Condensation of the 17α-ethynyloestradiol (CXXI) with formaldehyde and primary amines gave a mixture of two isomeric oxazines (CXXII) and (CXXIII), which are readily separated chromatographically[89]. Of the preparations obtained, the oxazine (CXIII; R = cyclohexyl) was a good anti-tumour agent. In large doses, all the compounds obtained exhibit oestrogenic action:



Reaction of 4β,5β-epoxy-5α-cholestan-3-one with 2-mercaptoethanol in dioxan in the presence of polyphosphoric acid gives cholesta-3,5-dieno[3,4-*b*]oxathian (CXXIV; X = O) in 78% yield and on reaction with ethanedithiol the dithian

(CXXIV; X = S) is obtained[90,91]. The oxathian (CXXIV; X = O) can to a certain extent be considered as a sulphur analogue of dihydro-oxazines of the type (CXXIII):



(CXXIV)

---o0o---

The information given in the present review shows that the recent rapid developments in investigations of the chemistry of heterocyclic derivatives of steroids are of definite interest in the chemistry of steroids as a whole. It can be hoped that further development of work in this direction will allow new biologically active compounds to be synthesised, which will evidently find use as pharmaceutical preparations.

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THE THERMOGRAPHIC STUDY OF POLYMERS

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I. INTRODUCTION

Thermography[1] — an effective method of chemical study — was until recently comparatively little used in the study of polymers. In recent years, however, a large and increasing number of papers have been published on the use of thermographic methods in the chemistry of macromolecular compounds, and this makes it desirable to review this work and to describe the possibilities and future prospects of this method. The chapter in Ke's book on newer methods of polymer characterisation[2] contains interesting material, but does not exhaust the subject.

In the thermographic method, the change in the temperature of a specimen placed in a heating block is recorded as the latter is smoothly heated (or, less frequently, cooled). Particularly valuable information is obtained by recording the difference in the temperatures of the specimen being studied and a standard substance placed in the same block, or the difference in the temperatures of the specimen and the block itself. The resulting differential curve shows, in the form of peaks or other deviations from a straight line, all the thermal effects and all changes in thermal characteristics leading to more rapid or less rapid increase in the temperature of the specimen relative to that of the standard, within definite temperature ranges. This method is called differential thermal analysis (DTA). This term is being used increasingly as a synonym for thermography.

Usually, both the temperature of the specimen ("simple recording") and the above temperature difference are recorded simultaneously with respect to a time coordinate. At the present time, however, many papers give only differential curves.

Thermographic studies are carried out using photorecording instruments of different designs, for example, the Kurnakov apparatus[3] and its various modifications[4,5]. Recording on electronic potentiometers (recorders) is now widely used. The sensitive elements are usually low-inertia thermocouples, but resistance thermometers and thermistors are sometimes used. A general trend is the reduction of the size of the specimen from the previously used gramme quantities to milligrammes or fractions of a milligramme[6] without decrease in the sensitivity of the analysis and with the production of more highly resolved peaks.

Thermography is one of the basic methods for the phase analysis and thermal characterisation of substances. It also provides a means of studying various transformations taking place in substances, such as the aging of alloys[7]. Thermograms can be used for the quantitative estimation of thermal constants (heat capacity, thermal conductivity[8]), and to determine not only the temperatures but also the heats of phase transformations and chemical reactions: for a given heat transfer coefficient, the heat of the process is proportional to the area of the peak described by the differential curve during the corresponding transformation[9]. Although the theory of thermal analysis is still being developed[10], the thermographic method has provided the basis of a number of methods of determining thermal quantities — methods combined under the heading of thermographic calorimetry[11] — and also as a basis for the production of suitable apparatus[12].

A characteristic feature of the thermographic method is that in some cases different physical and chemical processes (for example fusion, boiling, and endothermic reactions) produce identical effects. It is therefore the task — sometimes not easy — of the research worker to interpret the thermograms obtained. For this purpose it is often necessary to carry out additional experiments in which the substance being studied is subjected to various forms of heat treatment, after which the thermogram is recorded again. The introduction of data obtained by other methods is also extremely useful.

While noting the fact that thermographic methods are comparatively little used in organic chemistry, Ravich[13] correctly points out that this situation has developed both as a result of certain scientific traditions, and also because of the specific features of the materials studied; he refers to the complicated structures of organic substances, and their ability to undergo supercooling, vitrification, the formation of a large number of non-equilibrium systems, etc. A rational explanation of the discrepancies in the data obtained by different workers who apparently studied identical materials can be obtained only by making allowance for the time factor[14]. These features are even more characteristic of polymers.

The applicability of thermographic methods to the study of polymeric materials is related to their tendency to undergo various physical and chemical thermal transformations. The various chemical processes — polymer formation, vulcanisation, thermal oxidation, and degradation — are accompanied by definite thermal effects. The conversion of a polymer from the vitreous state into the highly elastic state is accompanied by a change in the thermal characteristics. Crystallisation, fusion, and polymorphic transformations are accompanied by the liberation or absorption of heat. Fig. 1 gives a schematic thermogram[15] which covers the complete temperature range of existence of a polymer and illustrates the manifestation of most of the above processes. It is naturally a general scheme, to provide guidance in the study of specific thermograms†.

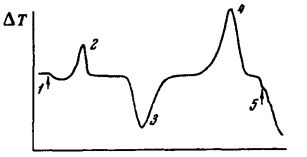


Fig. 1. Thermal processes in polymers (schematic):
1) vitrification; 2) crystallisation; 3) fusion; 4) oxidation; 5) degradation.

II. STUDY OF STRUCTURAL TRANSFORMATIONS

1. Thermographic Manifestations of Transformations in Homopolymers

In the study of polymers it is necessary to bear in mind the lack of correspondence between the structural and thermodynamic criteria of phase states[16]. X-Ray and crystal-optical methods give the structural characteristics of polymers, whereas thermographic methods give the phase characteristics.

Phase transformations characteristic of polymers include the formation of a crystalline phase from an amorphous phase (crystallisation) and the opposite process — fusion. For polymorphic crystalline polymers, interconversion of the modifications is also observed. The thermograms provide an objective representation of all these processes.

Vitrification. The conversion of vitreous polymers into a highly elastic or viscous-fluid state, and the opposite process, although they are essentially not phase transformations since they occur within a single amorphous phase, are accompanied by a change in a number of the properties of the polymers, including their thermal properties. As a result, despite the absence of the thermal effect characteristic of phase transformations, the thermogram shows a characteristic inflection: a change in the course of the differential curve from that characteristic of a polymer in the vitreous state to that characteristic of a polymer after softening. When the conditions of the experiment are unchanged, the magnitude of the inflection can be used to estimate approximately the quantity of amorphous phase in partly crystalline polymers.

Dudek and Lohr[17] used the thermographic method to study the vitrification temperature of poly(methyl methacrylate) and the influence of small quantities of monomer and plasticiser on this temperature. The vitrification of poly(methyl methacrylate) and atactic polypropylene was

† In all the Figures, as in most thermographic work, values of $\Delta T > 0$ (exothermic effects) are plotted upwards along the axis of ordinates, whereas values of $\Delta T < 0$ (endothermic effects) are plotted in the opposite direction. It should be borne in mind that a number of authors, chiefly foreign, use the opposite sign convention. Where their work has been used in the present review, the thermograms have been redrawn in accordance with the above principle.

studied by Strella [18], who proposed a method for calculating the heat capacity from the difference in the temperatures of the periphery and centre of a cylindrical specimen. This method was discussed and the calculation refined by Haly and Dole [19].

Wunderlich and Bodily [20] used "dynamic differential-thermal analysis", which makes it possible to compare a large number of thermograms recorded at different rates. They showed that for slowly annealed amorphous polystyrene the thermograms in the vitrification range show not simply the jump characteristic of the quenched specimen, but also a peak, which increases with the rate of heating. This method was also used to study the kinetics of the vitrification and softening of polystyrene [21]. Keavney and Eberlin [22], in a study of the vitrification of poly(vinyl chloride), polystyrene, etc., showed that change in the size of the specimen and the rate of heating has no significant influence on the transformation temperature T_g. Murphy [23] used a thermographic method to determine the dependence of the vitrification temperature on the molecular weight of polyacrylonitrile.

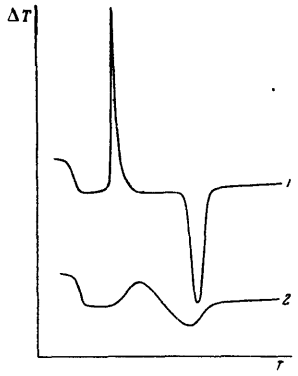


Fig. 2. Characteristic thermograms for an amorphous crystallising polymer: 1) with highly regular structure; 2) with lower regularity.

Crystallisation‡ can be observed on a thermogram if the rate of this process is commensurate with the rate at which the thermogram is recorded [25]. Since the thermogram usually covers an appreciable range of temperatures, the specimen during the experiment may find itself in a temperature range in which crystallisation takes place fairly rapidly; an exothermic effect will then appear on the thermogram. The absence of an effect from a given range does not indicate that crystallisation is not taking place. Thus the thermogram for amorphous natural rubber [26], which crystallises even at room temperature, does not show an exothermic effect in the corresponding range, since the process then takes place extremely slowly.

The intensity of crystallisation depends to a marked extent on the presence of crystalline nuclei in the bulk of the amorphous polymer [27]. Such nuclei may be provided, in particular, by traces of previously formed crystallites, which did not disappear completely when the polymer was converted into the amorphous state before the experiment. Sometimes, when the nuclei are removed completely, an exothermic effect may not appear on the thermogram, or the peak may be smaller and displaced towards higher temperatures.

Let us consider a polymer which is completely amorphous in the original state and which crystallises during the experiment (Fig. 2). The thermograms show a more or less sharp peak, whose area gives information on the integral heat liberation and hence on the total quantity of crystalline phase formed, and whose height gives information on the intensity of the process. A sharp high maximum indicates that all the material capable of crystallising has crystallised in a narrow time and temperature range ("explosively"). An equally sharp peak may be observed at a much higher temperature when the melt is cooled at the same rate. A broad range of intensive crystallisation is thus detected. The optimal temperature apparently lies in the middle of this range.

A high rate of crystallisation can be observed only in polymers with a highly regular structure. Decrease in regularity leads to a decrease in the rate of crystallisation, and the process then covers an appreciable temperature range. Considerable variations are observed in the degree of perfection or size of the resulting crystallites, and this is reflected in the considerable variation in their melting points. The temperatures of crystallisation and fusion of polymers differ considerably: definite melting points correspond to the observed temperatures of formation of crystallites [28]. This is also shown clearly on the thermograms. Illustrative data were obtained by Gray and Casey [29], who subjected polyethylene specimens, which had been converted into the amorphous form, to successive treatments at a series of decreasing temperatures. Each peak on the fusion thermogram corresponded to crystallites formed at a definite temperature (Fig. 3).

Fusion. In a thermographic experiment, crystallisation usually takes place at a continuously increasing temperature, and fusion also takes place continuously, over a wide temperature range. A flat exothermic crystallisation peak (curve *2* in Fig. 2) is often converted directly into an indistinct endothermic fusion minimum.

In many instances imperfect crystallites melt at temperatures favourable for subsequent crystallisation. Thus fusion is accompanied not only by formation of an amorphous phase but also by recrystallisation — the formation of more perfect crystallites melting at higher temperatures.

The dependence of the melting point on the rate of heating is due to two factors. The first of these — recrystallisation — tends to increase the temperature as the rate of heating is decreased, and is observed chiefly at low rates of heating. At rates of heating above a certain limit, the melting point is almost independent of the rate of heating [30] (it should be emphasised that here we are speaking not of

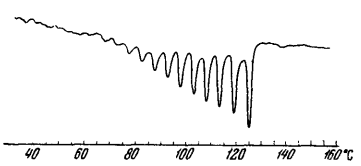


Fig. 3. Fusion of polyethylene crystallised at temperatures successively decreasing by 5 deg. [29]

‡ The crystallisation of polymers is discussed in detail in Mandelkern's monograph [24], but the thermographic method is not dealt with.

equilibrium fusion, but of metastable fusion). At high rates of heating, however, the second factor — superheating produced by kinetic factors — begins to operate in the opposite direction. It is here of interest to note the temperatures of three elements of the thermographic peak: the start, the peak value, and the end. For poly(tetrafluoroethylene)[31] at rates of heating reaching 46 deg min^{-1}, the superheating amounts to 30 deg, and is greater, the greater the molecular weight. The temperature of the start of fusion is independent of the rate of heating. At the intermediate rates used in thermographic studies, the possibility of superheating is small, and usually it is necessary to make allowance for the influence of only the first of the above factors.

The dependence of the temperature of the endothermic fusion peak T_{fusion} on the temperature at which crystallisation took place T_{cryst} (when almost no recrystallisation is observed during fusion) is close to linear (curve *1* in Fig. 4). The limiting melting point T_{lim} corresponding to the equilibrium crystals is characterised by the fact that the temperatures of crystallisation and fusion are equal. It can be found as the point of intersection of the extrapolated straight line giving the above relationship with a line drawn at an angle of 45° from the origin of coordinates ($T_{fusion} = T_{cryst}$). Using this method, Wyckoff[32] found the value 178.4° ± 0.3° for the limiting melting point of polypropylene. On recrystallisation, the curve giving the dependence of the melting point on the temperature of initial crystallisation undergoes a change in character; if the process took place under ideal favourable conditions, the crystallites formed at any temperature would reach the equilibrium state (line *2*). Usually, however, recrystallisation does not proceed to completion in a thermographic experiment, and the actual curve *3* lies between the two limiting straight lines.

Recrystallisation is revealed on the thermograms (Fig. 5) when the rate of this process is comparable to the rate of heating of the specimen during the thermographic experiment. Splitting of the fusion peak may be observed, due to superposition of the endothermic effect of fusion and the exothermic effect of crystallisation. By recording the thermograms at different rates, it is possible to observe a change in the ratios of the low-temperature and high-temperature peaks: the slower the rate of heating, the greater the relative magnitude of the latter. With very rapid heating, recrystallisation cannot take place at all. In this way it is possible to obtain proof that the splitting of the fusion effect is due to recrystallisation during the experiment. Frequently, however, the presence of two endothermic minima on polymer thermograms is due to other factors.

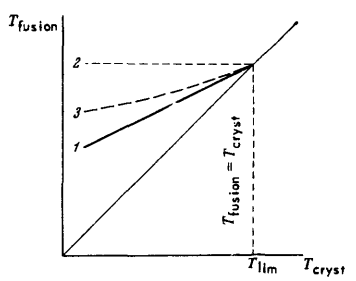


Fig. 4. Dependence of the melting point of a crystalline polymer on the temperature of crystallisation.

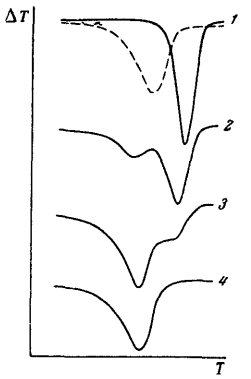


Fig. 5. Characteristic fusion thermograms for polymers in which the crystallites show a wide range of degrees of perfection. The rate of heating increases from 1 to 4; the broken line gives the hypothetical curve for where there is no recrystallisation.

Until now we have considered the thermograms of specimens in which the formation of crystalline phases takes place only during the actual thermographic experiment. Much more frequently, the crystallites in the specimens studied are formed at an earlier stage. The form of the thermogram then depends to a marked extent on the thermal pre-history of the material.

Since the crystallisation of a polymer can take place at a number of different temperatures, the crystallites obtained correspond to different endothermic peaks on the thermograms. For thermal analysis it makes no difference whether they correspond to different structural modifications (as for gutta-percha) or to crystallites of the same modification. This illustrates both the advantages and limitations of the thermographic method. On the one hand, it detects differences in super-molecular formations which cannot be detected even by X-ray diffraction. On the other hand, it cannot indicate whether the presence of two or more endothermic minima is due to differences in structure, recorded by X-ray diffraction, or to differences in the efficiency of aggregation. The existence of several endothermic effects with definite melting points (in the absence of polymorphic transformations) should not be regarded as an indication of the existence of the corresponding number of phases, since the crystallites of each type are not thermodynamically equivalent. Under favourable temperature conditions and over a sufficiently long period, they may all be converted into more stable crystallites with the "limiting" melting point. Thus the presence of these crystallites with different degrees of perfection, giving different peaks on the thermograms, is due not to thermodynamic but to kinetic factors.

Two or several fusion peaks are observed on a thermogram when the crystallisation has been carried out by treating the specimen at several gradually decreasing temperatures. On the other hand, when a specimen has been kept at several successively increasing temperatures, the thermogram shows only one endothermic peak, corresponding to the crystallites formed at the highest of the temperatures. (The previously formed low-temperature crystallites melt and undergo recrystallisation to different extents.)

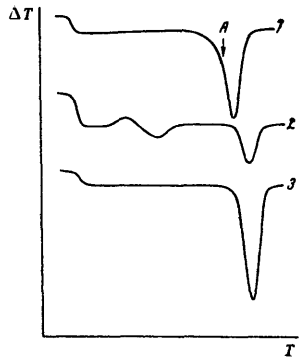


Fig. 6. Thermograms for crystalline polymers (schematic; see text for explanation).

If it can be assumed that the polymer has undergone recrystallisation, but that because of the relatively high rate of the thermographic experiment the process is revealed on the thermograms to only a very slight extent, it is best to treat the specimen in a special experiment for a more or less prolonged period at a temperature close to the melting point of the specimen, and then to verify, by repeating the recording, the efficiency of the recrystallisation process.

When non-equilibrium crystallites are heated for a relatively short period (at a temperature corresponding to point *A* on curve *1* in Fig. 6), only a small quantity of equilibrium phase is formed; the resulting amorphous phase is able to undergo only partial recrystallisation (the rate of crystallisation at this temperature is low), and can be detected in a subsequent experiment (curve *2* in Fig. 6): the thermograms show exothermic effects corresponding to the formation of new non-equilibrium crystallites from this amorphous phase, and the fusion of these crystallites. With increase in the duration of the constant-temperature treatment, the quantity of amorphous phase decreases and the quantity of equilibrium crystallites increases. The area of the peak and the peak temperature on the thermogram approach the limiting values (curve *3* in Fig. 6)[33].

Thus the thermographic method is extremely effective for the direct observation of the processes of crystallite formation and fusion in polymers, and also for phase analysis. It also reveals the thermal pre-history of a polymer specimen.

2. Thermographic Study of Individual Homopolymers

Early experimental results. The fusion and crystallisation of synthetic and natural polymers have been studied by a number of workers. Initially, the procedure used involved the construction of cooling and heating curves from data obtained by periodic temperature measurements (at isolated points). Baker and Fuller[34] and Jenckel and Wilsing[35] used this method to study crystallising polyurethanes and made a number of observations regarding the characteristic features of the fusion process, the dependence of the melting point on the conditions of crystallisation, etc.

The method of differential thermal analysis appears to have been used for the first time by Mikhailov and Klesman[36], who pointed out the characteristic features of the thermograms for two structural modifications of polyamides — crystalline and amorphous. They also undertook quantitative thermographic determinations of the heats of crystallisation and fusion of a polyamide of the polycaprolactam type. Even these early papers revealed the extensive possibilities provided by thermographic methods in the study of polymers, although the authors did not avoid a number of inaccuracies, in particular by attributing the endothermic effects to the conversion of the amorphous polymer from the vitreous state into the highly elastic state and from the highly elastic state into the viscous-fluid state. Subsequently, Mikhailov and Gorbacheva continued their studies of structural transformations in synthetic polyamides and polyesters[37], and studied the influence of the conditions of preparation, drawing, and heat treatment on poly(ethylene terephthalate) and fibres produced from it[38]. The same authors studied the influence of molecular weight (polycapramide and polypropylene), method of preparation — poly(vinyl alcohol) — and form (powder or fibre) (polyacrylonitrile) on the behaviour of polymers when heated[39]. Early work on the thermographic study of polymers includes Coste's work[40] on polyesters and polyamides.

Tolchinskii and coworkers[41] used the thermographic method to study polypropylene. They established the temperature limits of the crystallisation and fusion of the polymer, investigated the dependence of the crystallisation range on the rate of cooling, and estimated the degree of crystallinity of various polypropylene specimens.

Thermographic studies were also carried out by Ke, who examined various methodological features of the thermography of polymers and gave the differential-thermal heating and cooling curves for various grades of polyethylene, polypropylene, their mixtures[42], copolymers, and block-copolymers[43], and also the thermograms for various polyamides[44], polyesters[45], and other materials[46].

Polyalkenes. On the assumption that the heat of crystallisation of polyethylene is close to the corresponding value for hydrocarbons with sufficiently high molecular weight, Ke[42] determined the percentage crystallinity of this polymer by finding the ratio of the area of the peak on its thermogram to the peak area for dotriacontane, whose crystallinity was taken as 100%. The degree of crystallinity of polyalkenes was also determined by other workers. Thus Strella[47] describes the thermographic assembly, calculation procedure, and results obtained for crystalline polyethylene and polypropylene. On the basis of the theory that the heat capacities of the amorphous and crystalline sections of the polymer are additive, he used the experimental values of the deviations on the differential curve to calculate the degree of crystallinity for any temperature within the fusion range.

Wunderlich and Kashdan[49] studied specimens of polyethylene crystallised from the melt and isolated in the form of single crystals from solution. The degrees of crystallinity were compared by measuring the areas and heights of the thermographic peaks. In both instances good agreement with dilatometric data was obtained.

The slight lack of rigour in thermochemical calculations from the magnitude of the thermal effect of fusion is due to the fact that the conditions of the process are not isothermal. Chiu[50] described an assembly containing a heating block with two divisions. In the first of these the specimen is heated in the usual way until the required temperature is reached, after which it is immediately transferred to the second, constant-temperature division of the block, and the isothermal crystallisation curve is recorded.

The problems of the thermographic calorimetry of polymers have been examined by a number of authors[51,52]. The thermographic method has been used to study the kinetics of crystallisation of polypropylene[53] and to determine the temperature dependence[54] of the heat capacity of this polymer§. The crystallisation of polyethylene after partial fusion has been studied[55] and problems associated with the influence of the thermal history on the crystallisation of polyethylene have been investigated[56]. Similar problems have also been examined by a number of other workers[14,29,32,52,53,55]. Some thermodynamic aspects of the crystallisation of polyethylene and its copolymers have also been examined[57].

Baltenas and Igonin[58] found that for polyethylene specimens with different degrees of ordering the application of an external pressure of up to 3000 atm leads to an increase in the fusion range and to an increase in the temperature of the endothermic peak by 65–70 deg. This result shows the importance of the study of polymers under pressure; this aspect of thermographic studies has hardly been touched.

A number of factors influencing the shapes and dimensions of the elements of the fusion thermograms for polymers were studied by Ke[59]; he distinguishes factors which are determined by the characteristic features of the preparation of the specimens (the thermal history) and factors which are related to the characteristic features of the experimental procedure (size of specimen, rate of heating, method of introducing the thermocouples, etc.). Similar studies were made for synthetic fibres by Schwenker and Zuccarello[60]. As pointed out by Ke, the shape of the fusion peak gives information on the size distribution of the crystallites. The thermograms which he gives for random ethylene–propylene copolymers reflect the decrease in the percentage crystallinity and the decrease in melting point produced by introducing propylene units into the chain. The author explains this in terms of the effect of lateral methyl groups. In analogous situations, ethyl groups are even more effective. A similar phenomenon is also observed for copolymers of poly(ethylene terephthalate) and isophthalic acid; increase in the concentration of the latter in the copolymer to 40 mole % leads to complete suppression of crystallisation[45].

The thermograms for different crystallising polymers are in general of the same type. Thus the regular features noted for polyalkenes also characterise the thermograms for other classes of polymer.

Polyamides, polyethers, and polyesters. Inoue[61] studied the crystallisation and fusion of various polyamides, poly(oxymethylene), etc., in addition to polyethylene and polypropylene. A detailed study was made of Nylon-6; experiments were carried out to find how the crystallisation is influenced by the temperature of the melt, which determines the number of crystalline nuclei remaining (Fig. 7*a*). For Nylon-6 with high molecular weight and for poly(oxymethylene), two exothermic peaks are observed, attributable to the break in the rate of crystallisation with change in temperature. When a seed crystal is introduced, the crystallisation is complete at the temperature of the first peak (Fig. 7*b*). DTA data were used to estimate the heats of fusion and crystallisation of various specimens and to calculate their crystallinities.

§ The influence of nuclei on the crystallisation of polypropylene was recently studied by Beck and Ledbetter.[48]

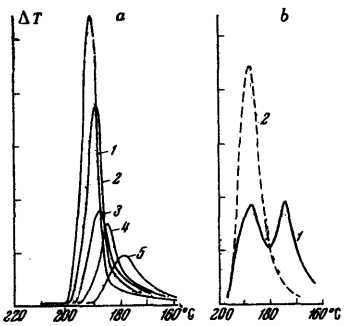


Fig. 7. Dependence of the crystallisation of Nylon-6 on:
a) the initial temperature of the melt: 1) 235°; 2) 245°; 3) 260°; 4) 290°; 5) 320°;
b) the presence (2) or absence (1) of nuclei-forming species.[61]

Gudim[62] used the thermographic method to study physical transformations in caprolactam and polyamide prepared by polymerisation in a vacuum, in an atmosphere of nitrogen, and in air, and also subjected to γ-radiation. The crystallisation and fusion of poly(ethylene terephthalate) were also studied[63]. Differential thermal analysis was used to study the properties of poly-β-propiolactone, prepared by polymerisation in the solid state[64].

The application of the method to organoelemental polymers has also been described[65].

Elastomers. Studies have been made of various forms of natural and synthetic elastomers (natural rubber, gutta-percha, and balata, and various grades of synthetic rubber), in which the fusion of the crystalline phase of the polymers and the conversion of the material from the vitreous state into the highly-elastic state were observed[66,67]. The influence of the rate of heating and the temperature of crystallisation on the melting point of rubber has also been noted[66]. The fusion ranges of the α and β forms of gutta-percha and the influence of the temperature of the melt on their ratio in the polymer were also studied.

Thermographic studies of natural rubber[69], gutta-percha[70], and synthetic chloroprene[71] and divinyl (SKD)[72] rubbers have been made by the authors of the present review. The vitrification, crystallisation, and subsequent fusion of rubbers which had been converted into amorphous forms have been studied, and the optimal crystallisation ranges have been determined. The areas of the peaks on the thermograms have been used to study the kinetics of the crystallisation of natural rubber and the way in which it is influenced by breakdown (milling)[73].

The thermograms of natural rubber show separate fusion peaks for crystallites formed at low temperatures (optimal crystallisation at -25°) and at room temperatures[69]. It has been established that the "high-temperature" crystallites act as nuclei for the low-temperature crystallisation; when the high-temperature crystallites are absent almost no exothermic effect is observed in the region of -25°.

For gutta-percha, cooling curves have been recorded in addition to heating curves. When melts obtained from the α or β forms of gutta-percha are cooled at medium rates, in every instance only the β form crystallises. When

the gutta-percha specimen is annealed at a temperature below the melting point of the β form, only the crystallites of this modification accumulate, whereas when the specimen is kept at a temperature slightly above the melting point of the latter, it is possible to obtain a material which exists almost entirely in the α modification[70].

Two specimens of highly regular divinyl rubber, containing 90% and 81% of the 1,4-*cis*-form, gave thermograms similar to those illustrated in Fig. 2 [72]. The extremely narrow crystallisation range of the first specimen results from the high degree of ordering and uniformity of the crystallites formed.

Recrystallisation processes are readily revealed on thermograms at rates of heating comparable with the rates of these processes. By annealing individual specimens of Nairit [neoprene type (Ed. of Translation)] at various temperatures, it has been possible to observe the increase in the degree of perfection of the crystalline phase and to obtain crystallites in a state close to the equilibrium state[71].

3. Thermographic Manifestation of Polymorphism in Polymers

Some crystallising polymers exist in various crystallographic modifications; we have already mentioned the α and β modifications of gutta-percha. When specimens which have been converted into the amorphous form are heated from low temperatures, the "low-temperature" less perfect form usually crystallises. Subsequently, when these crystals begin to melt, crystallisation of the second "high-temperature" form from the melt may be observed. In clearly defined instances the thermograms show a sharp exothermic effect which as it were separates the two peaks characteristic respectively of the fusion of each crystalline phase (curve *1* in Fig. 8). In less clearly defined instances the exothermic peak may not be so sharp, but the thermograms still show two minima or a "shoulder" on one side of the endothermic peak (curve *2* in Fig. 8). Finally, if the time required for the interconversion of the forms is very much greater than the time taken to pass through the corresponding temperature range in the thermographic experiment, the process is not observed at all on the thermograms. This is the reason for the fact that in the experiments referred to above the conversion of β-gutta-percha into the α form was not observed, whereas at extremely low rates of heating, which are very rarely used in thermographic studies, the thermograms reveal both forms[66,67]. The manifestation of polymorphism on the thermograms of *trans*-polybutadiene was observed by Dannis[68].

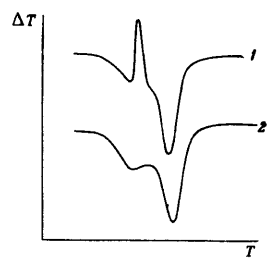


Fig. 8. Characteristic thermograms for polymers exhibiting polymorphism (see text for explanation).

Considerable attention has been paid to the study of the polymorphic transformations in polybut-1-ene, which exists in three modifications: their interconversions have been studied in detail[74]. The metastable tetragonal modification (form II) crystallises from the melt. Form III crystallises from solution. On its thermogram, the endothermic effect of fusion at 94° is converted into a sharp exothermic peak, which corresponds to the transformation of form III into form II. The second endothermic effect at 110° corresponds to the fusion of form II. Annealing of the specimen at appropriate temperatures increases slightly the melting point of each modification[75].

At room temperature, polybut-1-ene is gradually converted from form II into form I [76]; the rate of the conversion of form II into form I is much greater for specimens in the form of films than that for cast specimens[77]. The influence of traces of catalyst (ash) on the rate of the conversion of form II into form I was also studied. This conversion is irreversible[78]. The direct formation of form I during polymerisation has been described[79].

There is lack of agreement as to whether the transformation takes place with the formation of an intermediate melt or by a crystal–crystal scheme.

The phenomenon of polymorphism has been studied by the thermographic method for other series in addition to polyalkenes and dienes. Polyesters formed by adipic acid and *p*-phenylenebisethylene glycol, and also block-polyurethanes based on these materials[80], showed the existence of two polymorphic modifications, described as the α and β forms by analogy with gutta-percha. The heating curve for a polyester specimen which had been converted into the amorphous form and quenched revealed crystallisation of the β form at +12°. It begins to melt at 101–102°, but the exothermic crystallisation of the α form begins at 111°. This is followed by fusion of this form at 152°. The α form is obtained when a melt of the polyester is cooled slowly or when a specimen is subjected to constant-temperature treatment at 120–140°. The corresponding polyurethane which has been converted into the amorphous form crystallises in the β form at a slightly higher temperature and with a smaller thermal effect. The formation of the α form from this melt takes place less intensively, as indicated by the small exothermic crystallisation peak. The results obtained agree with data obtained by X-ray diffraction and infrared spectroscopy.

Of the other polymers, mention may be made of poly(tetrafluoroethylene), on whose thermograms Ke[46] observed two endothermic peaks at 20° and 29°, due to phase transformations in the polymer. The same result was obtained by Slonimskii and Ershova[81].

The thermographic method apparently detects not only the transformation of crystalline phases, but also some transformations in the vitreous state. Thus for polystyrene small thermal effects were observed at about 50°, attributed to hindering of the twisting vibrations of the phenyl groups[82].

4. Structural Transformations in Polymeric Systems

Berg[1], recommending thermography as a method for the phase characterisation of mixtures, points out that it is based on the fact that the temperatures of most phase transformations (and some reactions) are independent of the quantity and quality of the components in the mechanical

mixture. In solutions and alloys, however, the temperatures of phase transformations depend on composition, and thermographic study makes it possible to reveal this dependence. This is also true of polymeric systems, but there are additional considerations, related to the specific features of these materials. The phase analysis of polymeric systems in many instances gives quite definite results. The successful analysis of a mixture of seven polymers has been reported[83].

A random copolymer is a completely homogeneous system, which behaves like a homopolymer, with a characteristic set of properties; it is characterised by a definite vitrification temperature. For crystallising polymers, a decrease in crystallinity is observed on formation of copolymers, due to the non-regularity of the chain. This was examined above for the example of polyethylene containing propylene units. At a certain concentration of co-monomer, crystallisation may be suppressed completely, as mentioned above in connection with studies of polyesters[45]. It has been shown by DTA that polyethylene loses its ability to crystallise at a concentration of any of the co-monomers studied (methyl acrylate, methyl methacrylate, and vinyl acetate) of ~5.5 mole %[84].

Block and graft copolymers exhibit characteristic features which differ from those of random copolymers. In many respects they are similar to physical mixtures of polymers, for which the regular features of the thermograms are determined, as for any two-component or multi-component systems, by the phase equilibria: the presence and nature of ranges of separation into layers and crystallisation.

Systems formed by a polymer with a substance of low molecular weight. When a polymer and an inert filler are completely incompatible, the effects which they produce on the thermograms are completely independent and differ from those of the individual components only in their intensity. When the components are completely soluble (compatible) in the melt, crystallisation may lead to the formation of mixtures of the eutectic type, or solid solutions, and this, in accordance with the general principles of physicochemical analysis, determines the dependence of the melting points on composition.

Polymers which exhibit a limited compatibility with a substance of low molecular weight occupy an intermediate position. For crystalline polymers in these systems, the endothermic fusion peak is displaced usually towards lower temperatures. If the substance of low molecular weight is also crystalline, the thermogram also shows its characteristic fusion peak. This is illustrated in a paper by Ke[85]. The thermogram for a system in which the component with low molecular weight does not crystallise is shown in Fig. 9, and the thermogram for a system in which both components crystallise is shown in Fig. 10.

Polymer–polymer systems are characterised by thermograms which are determined in general by the same regular features. In the examination of mixtures of polymers, which may be obtained from compatible melts, solutions in a common solvent, or by milling, the question of the physical compatibility of the components of the mixture is of the greatest importance. This problem reduces to the determination of whether the system consists of one or several phases. In the first case the thermograms show one vitrification range and one range of crystallisation or fusion, whereas in the second (in principle at least)

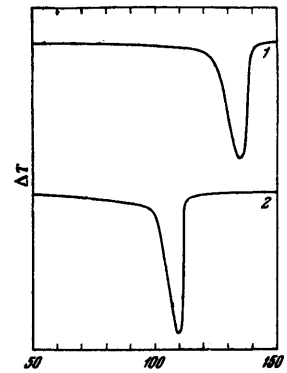


Fig. 9. Fusion of high-density polyethylene: 1) in pure form; 2) containing α-chloronaphthalene.[85]

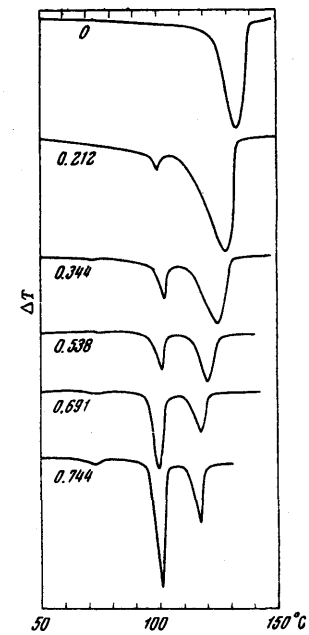


Fig. 10. Influence of phenanthrene on the fusion of high-density polyethylene. The figures next to the curves give the mole fractions of phenanthrene.[85]

the thermograms show several of these elements. Thermography thus provides a method for studying the compatibility of polymers. A study of this type was carried out by Mikhailov and coworkers[86] for the polyethylene–polypropylene system. The authors regarded the formation of two minima on the fusion curve as a criterion of incompatibility. Without objecting in principle to the conclusions reached here, we would point out that the formation of two minima is also observed for homopolymers, for which we cannot speak of compatibility. Thus the presence of several effects is a necessary but not a sufficient sign of non-homogeneity in a system.

Thermograms for the crystallisation of mixtures of the above system were given by Inoue[87]. A noteworthy feature is that the crystallisation of polyethylene and polypropylene takes place in the same temperature range. It

is natural that mixtures of these polymers should show a single crystallisation peak. Nevertheless, these polymers melt at different temperatures, and their non-homogeneous mixtures give separate fusion peaks on the thermograms [86,88].

In other examples the components of the mixtures may have identical melting points, and this feature must always be taken into account in the thermographic analysis of complex mixtures.

Mixtures of high- and low-density polyethylene give a homogeneous melt, but after the latter has solidified, the components melt separately, forming two peaks on the thermograms. An intermediate peak has also been observed [89], and on this basis an equilibrium diagram was constructed for the system, with an extended range of "mixed crystals" [90]. As shown above, however, not every thermal peak need be associated with a separate phase; it may be due to recrystallisation phenomena. A similar view is held by Gray and Casey [29], who consider that the intermediate peak results from annealing. Stafford [83] also studied mixtures of polyethylene with different densities by recording cooling (crystallisation) and heating (fusion) curves. He showed that the DTA method can be used for the quantitative analysis of mixtures.

Inoue [87] studied the crystallisation and fusion of mixtures of polyamides. The degree of crystallinity was determined from the peak areas, and it was concluded that a high degree of crystallinity is attained for the component present in excess. The decrease in the melting point (the peak value) observed for the high-melting component (Nylon-6) was almost imperceptible for the relatively low-melting component (Nylon-11). It should be noted that this last conclusion is not general, since changes in melting points are determined by the relationships between the components, responsible for the form of the fusion diagram of the specific systems.

Block copolymers. The thermograms of block copolymers show features characteristic of each of the polymers forming the blocks. If both are capable of crystallising, and the melting points are different, the thermograms show two separate fusion peaks, as for mechanical mixtures. For the ethylene–propylene block copolymer, Ke [42] showed the dependence of the magnitude of the peaks on the duration of annealing, and from the peak areas he estimated the proportion of each block in the total crystallinity. The same author observed a double exothermic crystallisation peak on the cooling curves, whereas a molten mixture of the corresponding homopolymers, in agreement with Inoue's data [87], gave only one unresolved peak.

Block and stereo-block copolymers with different compositions, obtained from the same components, have been studied [91]. It was found possible to determine the composition of the copolymers from the ratio of the areas of the fusion peaks on the thermograms (Fig. 11). Analogous studies were made by Porter and coworkers [92]. The quantity of crystallites corresponding to each block was found from the heights of the peaks on the thermogram. In spite of the arbitrary nature of this approach, it was found that the ratio of the height of the polyethylene peak to the sum of the heights of both peaks is an almost linear function of the weight fraction for mixtures and copolymers with different compositions. Over a considerable range of change in block ratios, the crystallinity of the copolymer is usually determined by the block present in excess. It is only in the range of comparable ratios that two systems of crystallites are observed simultaneously. This can be illustrated

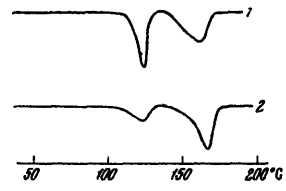


Fig. 11. Fusion of ethylene–propylene block copolymers:
1) 44 mole % ethylene; 2) 13 mole % ethylene. [91]

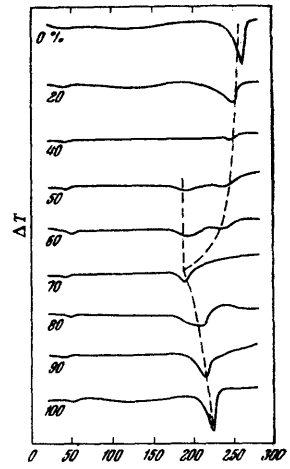


Fig. 12. Fusion of hexamethyleneadipamide–sebacamide copolymers for which a block structure was proposed. The figures next to the curves give the mole percentages of hexamethylenesebacamide. [44]

by an example [44] in which a study was made of poly(hexamethyleneadipamide–sebacamide) copolymers obtained by polycondensation at the phase interface (Fig. 12). The comparatively small displacement of the temperature peaks, shown by the broken line in Fig. 12, indicates, in the opinion of the authors, that the copolymers formed under the reaction conditions are block copolymers (random copolymers, in accordance with Flory's theory, give a much sharper decrease in temperature). The data given in Fig. 12 were used to construct a diagram resembling the eutectic fusion diagrams of binary systems. The "eutectic" composition corresponds to the copolymer containing 70% sebacamide. Block copolymers of the same adipamide with terephthalamide gave a diagram of the non-eutectic type, and this was attributed to the possibility of mixed-crystal formation.

Thermographic studies have been made [93,94] of model block polyesterurethanes, in which one block consisted of an aliphatic polyester and the other consisted of an arylene-containing polyester. The thermogram for a polymer consisting entirely of non-crystallising blocks showed only a jump at the vitrification temperature, after which the differential curve rose very slowly. As the percentage of crystallising blocks was increased, the effect of fusion was

revealed with increasing clarity (the effect is complex due to recrystallisation). In a series of copolymers for which both blocks are capable of crystallising, the regular features observed are similar to those described above for polyamides. In some instances the thermograms were complicated by the phenomenon of dimorphism, characteristic of the polyesters[80].

III. STUDY OF CHEMICAL REACTIONS

1. Thermal Reactions of Polymers

Vulcanisation, isomerisation, and thermal oxidation and degradation are all reactions which can be revealed by thermograms. All these processes are exothermic, except the last: degradation is usually accompanied by absorption of heat. Frequently, it follows one of the other processes (most frequently thermal oxidation) and the exothermic effect is converted into the endothermic effect, just as was observed in the range of crystallisation and fusion of crystals. These effects are observed at much higher temperatures, however, and there is usually no difficulty in distinguishing them. The extent of the exothermic range and the sharpness of the transition from oxidation (or other exothermic process) to degradation is determined by the nature of the polymer, the presence of stabilisers, and the nature of the surrounding atmosphere.

The transformations of phenol–formaldehyde resins were observed by Ravich and coworkers[13]. The exothermic effect at 165° for Resol corresponds to its conversion into Resite, whose thermogram does not show this effect. DTA was used to study[95,96] the vulcanisation of Vibrin-135 — a mixture of poly(glycol maleate) and triallyl cyanurate polymer. The exothermic peak in the range 150–180° corresponds to polymerisation at the double bonds of the polyester and the second allyl group of triallyl cyanurate. The exothermic effect at 300–320° is due to the polymerisation of the third allyl group.

The curing of a large number of commercial products — unsaturated ester resins and epoxide resins — has been studied[97], but the results given are not sufficiently definite. When epoxide compounds react with anhydrides and diamines, an exothermic peak is observed in the range 100–150° (at lower temperatures for the former than for the latter, due to the greater reactivity)[98]. The exothermic peak at 300–400° is considered to be due to the isomeric conversion of the epoxy-groups into carbonyl groups and the start of decomposition.

Unsaturated polyester–styrene copolymers have been studied[99]. The ratio of the exothermic peak areas for specimens cured at room temperature for different periods of time to the peak areas for a specimen studied immediately after preparation provided a measure of the degree of curing (Fig. 13). A similar method was used to study the cure rate of phenol–formaldehyde resins[100]. The rate of vulcanisation of rubber by sulphur has been studied[101] by recording the thermograms for specimens subjected to preliminary partial vulcanisation in a press for different periods of time at 153°. The influence of metal oxides on the vulcanisation of ebonite was also studied[102]. A modification of the thermographic method, which makes it possible to determine the heats of vulcanisation of rubbers, has been proposed[103]. The vulcanisation (under the influence of diamine, benzyl peroxide, or magnesium oxide) of the copolymer of vinylidene fluoride with perfluoroprene

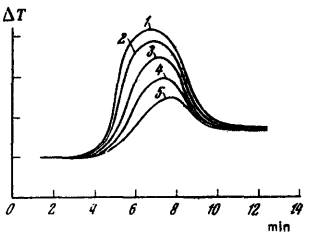


Fig. 13. Polymerisation during the heating of unsaturated polyester–styrene copolymers after hardening for:
1) 2; 2) 3; 3) 4; 4) 5; 5) 6 h.[99]

has been studied, but the thermograms obtained do not appear sufficiently significant[104].

In principle, the thermographic method can also be used to study various polymer-analogue transformations and other reactions taking place with the participation of macromolecular compounds. The thermal effects in the reaction mixtures are studied. Mention may be made of a unique application of the method to study the processes taking place in the water–heat treatment of starch[105,106].

2. Thermal Degradation

Thermographic methods are often used to estimate the thermal stability of polymers. The results of a thermographic experiment differ considerably from the data obtained by prolonged treatment of a polymer at elevated temperatures. This is due to the fact that the thermographic experiment, with its characteristic dynamic temperature conditions, lasts for only a short period and a measurable degree of degradation may be reached at higher temperatures than under the conditions of static tests. Moreover, the shape of the thermogram often depends on the dimensions and shape of the specimen and its degree of dispersion (block or powder), and also on the nature of the surrounding atmosphere. For comparative purposes, however, for example the comparison of a series of specimens, or the study of the influence of stabilisers or other ingredients, the thermographic method can prove extremely useful.

The thermographic method may give information on the mechanism of degradation of polymers. Thus the method has been used to study the degradation of polyethylene (high- and low-density) and polypropylene; it was found that degradation is preceded by oxidation with the formation of hydroperoxides[107]. The thermal behaviour of isotactic polypropylene has also been studied[108]. DTA has been used to investigate the influence of antioxidants on the thermal stability of polyethylene[109].

The thermal transformations of poly(methyl methacrylate), polystyrene, and phenol-formaldehyde resins have been studied[110]; effects associated with degradation of the polymers and secondary decomposition of the breakdown products were observed.

Lee[111] used a variety of methods to study the thermal stability of polycarbonates, and gave the characteristic thermogram for lexan. He considers that the exothermic peak at 300–320° corresponds to oxidation (it almost disappears in an atmosphere of nitrogen), and that the endothermic peak at 340–380° is due to depolymerisation

resulting from reactions such as the separation of hydroperoxides, hydrolysis, the separation of bisphenol, and alcoholysis. The processes of thermal degradation begin at higher temperatures: decarboxylation, dehydration, hydrolysis, dehydrogenation, chain rupture, and the separation of ester (together with possible formation of cross-linkages). With heating in air, these processes correspond to the endothermic peaks at 450–600°. Lee points out that since the initial step in the degradation is oxidation, this process should be inhibited to increase the stability of the polymer, but "pure" degradation may be observed independently of oxidation at higher temperatures. The degradation of block copolymers based on polycarbonate has been studied[112].

Korshak and coworkers studied polybenzimidazoles[113,114] and a number of polyarylates[115], which were shown by thermographic analysis to have a high thermal stability. The temperatures of the start of decomposition of the polyarylates lie in the range 375–465°, and those of the polybenzimidazoles lie in the range 460–520°. Mixed polybenzimidazoles (the diphenyl esters of a mixture of sebacic or terephthalic and isophthalic acids) show a slightly lower thermal stability than the homopolymers. Heat-resistant triazole polymers[116], hexa-allylmelamine polymers, and certain related compounds[117] have been studied.

Studies have been made of the thermal stability, characterised by the temperature where oxidative processes start, for some silicone polymers[118]. Pashchenko[119] has studied organosilicon compounds used as lacquers.

In a study of polymers with inorganic main chains, Andrianov[120] concluded, on the basis of DTA data, that cyclic compounds containing Si, Al, Ti, and Co atoms joined through oxygen have a high stability to elevated temperatures. Opening of the rings takes place above the temperature corresponding to the stability of the organic groups framing the inorganic part of the molecules.

Thermographic methods have been used[121] to study the compatibility of polymethyl methacrylate and octadecylammonium bentonite filler. The latter shows an exothermic effect on the thermogram at 285°, corresponding to the combustion of its organic fraction. This peak is completely suppressed in the presence of 10% poly(methyl methacrylate); the authors regard this as evidence for the compatibility of the polymer and filler.

Studies have been made of the processes taking place when SKN-40 nitrile rubber and phenol–rubber compositions based on it are heated[122]. For SKN-40, an exothermic effect begins at 250°, attributed to rearrangement of the internal structure and the formation of bridges between the molecules. Weight losses are observed above 360° due to oxidative thermal degradation.

The thermal analysis of some polyurethane elastomers[123] and polyester resins[15,124] has been carried out. The stability of a number of fibre-forming polymers has been studied[60] and it has been established that Nylon-6 and polypropylene give only endothermic peaks, indicating depolymerisation, whereas polycarbonate (lexan) and Teflon show both exothermic and endothermic peaks on the thermograms in the degradation range. The thermographic method has been used to study the pyrolysis of wood and its components[125]. DTA has been used to study the influence of inhibitors on the pyrolysis and combustion of α-cellulose[126]. Wood gives an interesting thermogram, which appears as the superposition of the thermograms of its main components — cellulose and lignin. A considerable number of thermograms of natural substances (celluloses, starches, and related compounds) have been published[127]. Studies have been made of the thermal stability and flammability of phenol and epoxide resins used as fillers for paper[128].

It is clear from a large amount of experimental material that the final stage in the recording of the thermograms may be the complete volatilisation of the degradation products (with an endothermic effect), or their combustion (with a sharp exothermic effect), or finally carbon formation, depending on the nature of the polymer and the conditions of the experiment. For an intensive study of the mechanism of degradation it is desirable to combine thermographic methods with study of the change in the weight of the specimen (thermogravimetric studies) and analysis of the decomposition products, for example by chromatography, mass-spectrometry, etc.

3. Reactions of Polymer Formation

A unique application of the thermographic method is in the study of the kinetics and mechanism of the reactions of polymer formation, since these processes involve the liberation of heat.

The thermographic method appears to have been first applied to the study of polycondensation by Brasseur and Champetier[129–131]. In the reaction of ethylene glycol, glycerol, and other polyhydroxy-compounds with phthalic anhydride, the endothermic effect due to fusion (dissolution) of the anhydride is followed by an exothermic maximum due to polyesterification; the water produced at this stage reacts with the excess of anhydride to form the acid. It is only at higher temperatures that the esterification of the dihydroxy- or polyhydroxy-compound by the acid produced leads to the liberation of water; the thermogram then becomes irregular due to the formation of bubbles of water vapour at the thermocouple. If acid is taken at the beginning of the reaction, no exothermic peak is observed on the thermogram.

Thermograms obtained in a study of the formation of phenol–formaldehyde resins[132] showed exothermic effects due to condensation of the original reagents (60–110°) and curing of the resulting resins (168–180°). It is of interest to compare the thermograms recorded at different component ratios (Fig. 14). The thermographic method has been used to study the formation of alkylphenolic resins[133].

The thermographic method has also been used to study the mechanism of polymerisation[134] for triallyl cyanurate and triallyl isocyanurate. Triallyl cyanurate gives peaks at 100° and 160–220°. The first was attributed to the reaction of two of the double bonds, and the second to polymerisation at the third double bond with the simultaneous

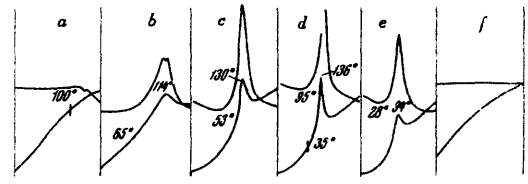


Fig. 14. Action of heat on phenol–formaldehyde mixtures with phenol concentrations (%):
a) 10; *b*) 30; *c*) 58; *d*) 80; *e*) 90.[132]

conversion of cyanurate into isocyanurate. In triallyl isocyanurate all the double bonds are polymerised at the temperature of the first exothermic peak.

The formation of macromolecular compounds by polymerisation under the influence of radiation has been studied. Since the process is exothermic, it has often been studied by measuring the increase in temperature in general [135] and by the thermographic method in particular. In the study of the polymerisation of formaldehyde in the solid state under the influence of γ-rays [136], it was found that at certain temperatures and intensities of irradiation the reaction acquires the character of a thermal explosion. The analogous reaction of acetaldehyde has also been studied [137].

DTA has been used to study the polymerisation, initiated by irradiation, of cetyl methacrylate, *N*-methylsuccinimide, and *N*-vinylcaprolactam in the solid and liquid states [138]. The reaction takes place smoothly or explosively, depending on the conditions. The radiation polymerisation of crystalline trithiane has been studied [139].

Kargin and coworkers [140-142] used the thermographic method to study the polymerisation taking place when certain monomers were heated below their melting points in the presence of magnesium vapour as initiator. They noted that this process takes place at temperatures close to the phase transformations of the monomer and is explosive in character. Thus the thermogram for the acrylonitrile–Mg system shows "spikes" on the differential curve at -165° or -135°. These temperatures correspond to exothermic maxima on the thermogram for pure acrylonitrile.

In the works cited, the thermographic method was used for the direct observation of polymerisation in the solid state, but it has also been used to characterise the polymers obtained [143].

IV. THERMOGRAPHY AND RELATED METHODS OF STUDY

The thermogravimetric method. The method involving the periodic weighing of a specimen kept at a definite temperature is often used to estimate the thermal stability of a polymer and to study the kinetics of its decomposition. The automatic recording of the change in weight in a controlled atmosphere, particularly under vacuum, both under isothermal conditions and with regular increase in temperature, has undoubted advantages [144]. In the latter circumstance the thermal conditions correspond to those used in the thermographic method, so that it is possible to record thermographic and thermogravimetric curves simultaneously; this method is used in the study of minerals [145]. The assembly may also record the linear contraction of the specimens [146] (see also Mashintsev and coworkers [147]). In another successful development [148], the apparatus records not only the simple and differential temperature curves and the weight curve, but also a differential curve characterising the rate of change in weight. This apparatus has been called a derivatograph.

Thermography with recording of the gas liberation. The formation of gas during the thermal degradation and certain other reactions of polymers makes it possible to study these processes from the dynamics of gas liberation. Both manometric [149,150] and volumetric methods can be used. An advantage of the volumetric method over the manometric method is that the pressure is kept constant, so that it does not oppose the reaction. The combination of the thermographic method with automatic recording of the gas liberation was developed for substances with low molecular weights [151], but it can also be applied successfully to polymeric materials. The possibility of carrying out the recording at reduced pressure is extremely valuable [152]. Although this method has not yet been applied to polymers, we would like to point out its promising possibilities. It should be noted that the volumetric and thermogravimetric methods do not always give concordant results. For example, in the degradation of polymers the gases and non-condensing vapours form only one source of the loss in weight; condensing volatile decomposition products do not produce a change in volume.

The combination of thermographic methods with mass-spectrometry is extremely fruitful. Under smooth heating conditions, it is possible to record the thermograms and either to obtain the mass spectrum (with rapid scanning) at various temperatures or to record continuously the ion current — either the total current or the current corresponding to a given ion, for example H_2O^+ (m/e = 18). In one scheme [153] a milligramme specimen is placed in a miniature furnace mounted directly in the ion source of a mass-spectrometer of the time-of-flight type. The decomposition is carried out under the extremely high working vacuum conditions of the instrument (about 10^{-7} mmHg). In another development [154], the gases formed on decomposition pass into the mass-spectrometer along a tube from a removable heating block in which any desired pressure can be maintained. In the latter case, however, retardation of the mass-spectrometric peak relative to the thermographic peak may be observed, the retardation being greater, the higher the pressure and the greater the "dead volume" of the system. This method, which has been tested for substances of low molecular weight, appears quite promising for the study of polymers. The same is true of the combination of thermographic methods with gas chromatography.

Thermography combined with microstructural studies. The thermograms for micro-quantities of a substance can be recorded directly on a microscope slide, heated by a linear programme on a special heated microscope stage [155]. It then becomes possible to make simultaneous observations, to take photographs at intervals, or even to record a cine-film. A correlation is thus established between the structural changes observed in the microscope and the thermal effects on the thermogram. This method, which has been used successfully, in particular, to study the phase structure of triglycerides, also appears promising for the study of polymeric materials. The combination of the widely used microscope observation of structures and their transformations with thermographic characterisation of the polymers appears extremely promising.

Thermographic and thermomechanical methods for studying polymers. Thermomechanical curves [157] are widely used in the study of polymers [158]. The method most similar to the thermographic method is that in which the temperature is altered by a linear programme and the deformation of the polymer takes place under the influence of a continuous load [159]. Automatic recording of the deformation on deformation–time coordinates or, more particularly, deformation–temperature coordinates [160,161] makes it possible to compare the curves obtained with thermograms recorded under the same thermal conditions. An assembly has been described, in which the

specimens used to obtain the thermograms and thermomechanical curves are heated simultaneously in the same block.

The thermomechanical curves for amorphous polymers can be used to determine the temperatures of vitrification and flow. The thermograms give the vitrification point but do not reveal the point corresponding to conversion into the fluid state. The thermomechanical curve records any change in the state of the polymer, if this change is associated with a change in its deformability (under a varying load)[162]. The thermographic method records a change in the state of the substance through its thermal properties, and the thermomechanical method records a change in state through the mechanical properties. In specific instances these methods may show different sensitivities to a change in state, so that the two methods supplement one another.

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KINETICS AND MECHANISM OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES UNDER THE CATALYTIC ACTION OF SULPHURIC ACID AND OLEUM

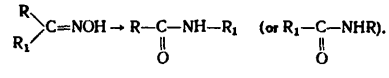
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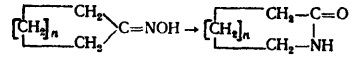
I. INTRODUCTION

In 1886 Beckmann[1] first carried out the conversion of oximes into acid amides. This reaction is called the Beckmann rearrangement. In the rearrangement of the ketoximes *N*-substituted amides of carboxylic acids are formed:



The Beckmann rearrangement was at first used only under laboratory conditions as a convenient and simple preparative method and as a method for establishing the structure of ketones. This reaction made it possible to synthesise a large number of amides, and also various amino-acids, which either were unknown or were obtained by complex processes of poor efficiency.

Recently the Beckmann rearrangement of a series of cyclic aliphatic ketoximes has attained great importance as an industrial method of obtaining lactams:



The rearrangement of cyclohexanone oxime into ϵ-caprolactam is of special importance. The industrial production of the lactam of ϵ-aminocapronic acid is one of the multi-tonnage processes of contemporary chemical industry. Wallach[2] obtained ϵ-caprolactam from cyclohexanone oxime under the catalytic action of sulphuric acid in 1900. ϵ-Caprolactam is the raw material for the production of one of the most important products of contemporary synthetic chemistry — caprolactam polyamide.

Lactams with a greater number of carbon atoms than ϵ-caprolactam also find application in industry, since they have been used as the basis of syntheses of polyamide resins with different physicochemical and mechanical properties.

The Beckmann rearrangement is an acid–base process and proceeds under the catalytic action of a large quantity of the reagents. The catalysts for this reaction are protic and aprotic acids. Concentrated sulphuric acid is usually employed, but phosphoric acid, phosphorus pentachloride, aryl sulphonyl chlorides, aluminium chloride, hydrogen bromide, and hydrogen fluoride are also used as catalysts. "Beckmann mixture" is an active catalyst for the rearrangement; it consists of a saturated solution of hydrogen chloride in glacial acetic acid, to which is then added ~ 20% acetic anhydride. This reagent is used under conditions when the oxime reacting is insoluble in other solvents.

Because of the great theoretical and practical interest of the Beckmann rearrangement, the literature devoted to an explanation of its mechanism is voluminous. There are

now over six hundred papers on the Beckmann rearrangement of various ketoximes and aldoximes. The most important information on this subject has been surveyed in detail in the review articles of Jones[3], Knunyants and Fabrichnyi[4], Donaruma and Heldt[5], and Zil'berman[6], and in Houben-Weyl[7].

Unfortunately, among the many publications devoted to the study of the mechanism of the Beckmann rearrangement, very few are of a quantitative nature. However, the ideas developed on the basis of synthetic data and also on the structure of the final and intermediate products of the rearrangement are undoubtedly of interest; such data are quite valuable for understanding the mechanism of the reaction.

The present review considers the kinetic data and mechanism of the Beckmann rearrangement of alicyclic ketoximes in aqueous solutions of sulphuric acid and in oleum. Sulphuric acid and solutions of sulphur trioxide in sulphuric acid are effective catalysts of this process; they are used in the industrial manufacture of ϵ-caprolactam. Parameters are known for these solutions which characterise the thermodynamic and catalytic properties used for establishing the mechanism of ionisation of the reagents and the mechanism of the limiting stage of the chemical process.

II. SOME PROPERTIES OF CONCENTRATED AQUEOUS SOLUTIONS OF SULPHURIC ACID

The Hammett acidity function H_0, the thermodynamic activity of the acid a_{HA}, and the thermodynamic activity of the water in the acid a_{H_2O} are quantitative characteristics of the catalytic activity of aqueous solutions of strong acids. It should be noted that in an investigation of the detailed mechanism of chemical reactions in acid media and particularly their early stages, a knowledge of the accurate values of H_0, a_{HA}, and a_{H_2O} of the solution in which the reaction is proceeding becomes particularly important. Fig.1 gives the values of H_0, $a_{H_2SO_4}$, and a_{H_2O} at 25° for concentrated aqueous solutions of sulphuric acid and dilute oleum. The values of $a_{H_2SO_4}$ were taken from Giauque and coworkers[8], the value of H_0 from Vinnik and coworkers[9], and the activity of water from Giauque and coworkers[8] and Vinnik and Ryabova[10].

The ionic and molecular compositions of aqueous solutions of sulphuric acid are also known[11,12]. Information about the equilibrium composition of the solution is needed to explain the mechanism of the physicochemical interaction of the reagent with the medium. The following species are in equilibrium in aqueous solutions of sulphuric acid: undissociated sulphuric acid H_2SO_4, the anions HSO_4^- and SO_4^{2-}, and also the ion pair $HSO_4^-.H_3O^+$ (or the hydrate of the acid $H_2SO_4.H_2O$). Fig. 2 shows the concentration of the ions HSO_4^- and SO_4^{2-}, the undissociated H_2SO_4 molecules, and the ion pairs $HSO_4^-.H_3O^+$ (or the species $H_2SO_4.H_2O$) as a function of the sulphuric acid concentration, after Zarakhani and Vinnik[12]. In dilute aqueous solutions of sulphuric acid, alicyclic oximes undergo hydrolysis. In aqueous solutions of the acid with >85–90% H_2SO_4, oximes are almost completely converted into lactams. As will be shown below, the rate constant of the Beckmann rearrangement increases with the concentration of the acid in the interval 85–100% H_2SO_4. In very dilute oleum the rate constant rises with increase in the concentration of sulphur trioxide in the solution. For these particular solutions the following

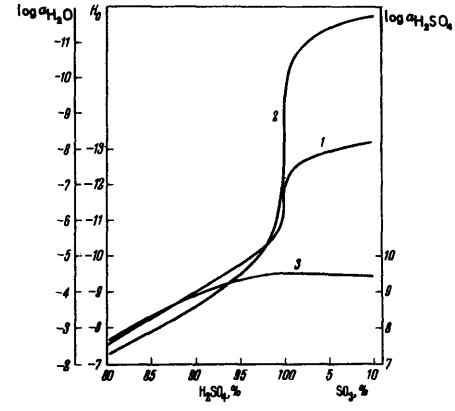


Fig. 1. Thermodynamic activity of water and acid and acidity function of concentrated aqueous solutions of sulphuric acid at 25°:
1) H_0; 2) $\log a_{H_2O}$; 3) $\log a_{H_2SO_4}$.

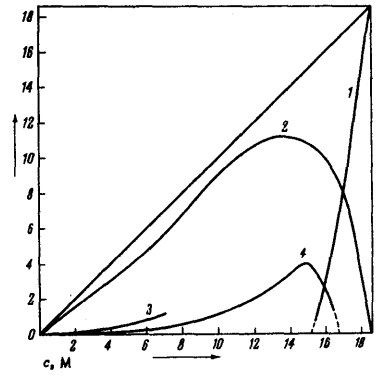


Fig. 2. Concentrations of ions and species in aqueous solutions of sulphuric acid:
1) H_2SO_4; 2) HSO_4^-; 3) SO_4^{2-}; 4) $HSO_4^-.H_3O^+$.

regularities are observed in the change of the parameters listed above. As the concentration of the acid is increased the acidity of the medium rises, the acidity function H_0 falls ($H_0 = -\log h_0$), the thermodynamic activity of the acid rises, and in the range 99–100% H_2SO_4 it is almost constant; the thermodynamic activity of water falls; the concentration of the HSO_4^- anions also decreases.

In oleum, as the concentration of sulphur trioxide is increased the concentration of the $H_3SO_4^+$ and $HS_2O_7^-$ ions rises but the concentration of the HSO_4^- anions falls[10]. The water activity a_{H_2O} also falls[10]. The activity of sulphuric acid $a_{H_2SO_4}$ in oleum falls — on account of the bonding by sulphur trioxide into pyrosulphuric acid and of ionisation, but apparently the decrease is slight.

III. SOME INFORMATION ABOUT THE MECHANISM OF IONISATION OF ALICYCLIC KETOXIMES IN AQUEOUS SOLUTIONS OF STRONG ACIDS

In acid solutions oximes are present in various forms coexisting in equilibrium. This has been shown by kinetic experiments on the hydrolysis of oximes in dilute aqueous

solutions of sulphuric and hydrochloric acids and also from information on the effect of additions of oxime on the acidity of concentrated solutions of sulphuric acid. As the concentration of the acid is increased, the effective rate constant of the hydrolysis of cyclohexanone oxime[13] and cyclopentanone oxime[14] at first rise, reach a maximal value, and then fall sharply. The maximal value of the rate constant of the hydrolysis is observed in extremely dilute solutions of the acid (see Fig. 3). For example, with cyclohexanone oxime the maximal rate constant is reached in 4.65×10^{-3}–6.52×10^{-3} M solutions of hydrochloric acid[15] and in 1.39×10^{-3}–5.2×10^{-3} M solutions of sulphuric acid[13]. The increase in the rate constant of the hydrolysis is connected with the appearance of reactivity in the protonated form of the oxime† $RNOH_2^+$:

$$RNOH + H^+ \rightleftarrows RNOH_2^+.$$

The decrease in the rate constant of the hydrolysis in such dilute solutions of acids can be explained only by change of the protonated form of the oxime into an unreactive form during the hydrolysis of the ion pair $RNOH_2^+.A^-$:

$$RNOH_2^+ + Cl^- \rightleftarrows RNOH_2^+ \cdot Cl^-,$$

$$RNOH_2^+ + HSO_4^- \rightleftarrows RNOH_2^+ \cdot HSO_4^-.$$

Hence from data on the dependence of the rate constant on acid concentration it follows that in aqueous solutions of strong acids alicyclic ketoximes are present in at least three forms: un-ionised RNOH, protonated $RNOH_2^+$, and ion pairs $RNOH_2^+.HSO_4^-$. The ion pair can also be named as a salt of the oxime‡. Calculations based on the data from hydrolysis show that alicyclic ketoximes are very strong bases. For example, cyclopentanone oxime and cyclohexanone oxime are already completely protonated in 0.05 *N* sulphuric acid[13,14] and hydrochloric acid[15] solutions. In more concentrated solutions the protonated form is completely converted into ion pairs. Cyclohexanone oxime in 2.5% H_2SO_4[13] and cyclopentanone oxime in 10% H_2SO_4[14] are found almost completely as the ion pairs $RNOH_2^+.HSO_4^-$. However, owing to the change in the activity coefficients of the ion pairs and protonated species in highly concentrated H_2SO_4 solutions, dissociation of the ion pairs occurs with formation of protonated species $RNOH_2^+$. For example, in 99% sulphuric acid the ion pairs of suberone oxime are completely dissociated and almost all the oxime in solution is present as the ions $RNOH_2^+$.

This conclusion is based on experiments on the influence of additions of oxime on the acidity of sulphuric acid solutions. In highly concentrated sulphuric acid small quantities of the dissolved substance change the acidity of the medium differently according to whether protonated species or ion pairs are formed. A change in the properties of the medium is reflected in the degree of ionisation of indicators used to measure the acidity function.

Water is known to be completely ionised in sulphuric acid solutions with >90% H_2SO_4:[16]

$$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-.$$

† Here and subsequently the following symbols are used: un-ionised form of oxime, RNOH; protonated form of oxime, $RNOH_2^+$; salt of oxime, $RNOH_2^+.A^-$; dehydrated salt, $RN^+.HSO_4^-$.

‡ The structure of the complex which consists of the protonated form of the oxime and the anion of the acid is unknown. It can be either an ion pair (a salt), or an ester of the oxime and sulphuric acid.

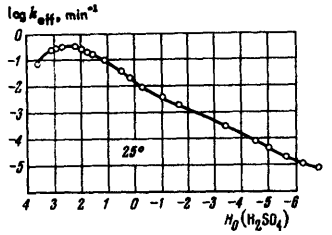


Fig. 3. Variation of the rate constant of the hydrolysis of cyclohexanone oxime with the acidity function H_0 of sulphuric acid.

TABLE 1. Effect of additions of suberone oxime on the ionisation of 2,4,6-trinitroaniline at 25°†.

H_2SO_4 concn., wt. %	Acid taken, g	Oxime added, g	$\log c_B/c_{BH^+}$ of indicator	H_0	H_0^*
99.145	6.684	—	—0.68	—10.64	—
	6.684	0.0868	—0.58	—10.54	—10.56
	6.684	0.281	—0.42	—10.38	—10.40
	6.684	0.413	—0.33	—10.29	—10.32
	6.684	0.544	—0.26	—10.22	—10.23

† H_0^* is the acidity function of a solution of 99.145% H_2SO_4 to which instead of the oxime an equal number of moles of water are added.

When the test substance changes the acidity function of the solution as does an equimolar amount of water, then it is present completely as the protonated form. When ion pairs are formed the change in the acidity function will be less than in the dissolution of the same number of moles of water. This criterion can be used to study the ionisation mechanism in 98–100% sulphuric acid where it is possible to use such small additions of the substance that concentrations can be used instead of activities in the expression for the equilibrium constant. Table 1 gives values of the acidity function for 99.145% acid with addition of suberone oxime. 2,4,6-Trinitroaniline was used as the indicator in measuring the acidity function. Relatively small additions of the oxime (up to 1 M) alter the acidity function of the medium by the same amount as equimolar additions of water. Consequently, oximes are present in these solutions as the protonated species $RNOH_2^+$.

IV. RATE CONSTANTS OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES

In connection with the analysis of kinetic data on the Beckmann rearrangement it is desirable to note which methods are used to determine the degree of conversion of oxime into lactam. In some published works the degree of conversion of oxime into lactam was determined from the quantity of unreacted oxime. Wichterle and Roček, in an investigation of the Beckmann rearrangement of cyclohexanone oxime in oleum[17–19], determined the concentration of oxime in the specimens by a colorimetric method[20], based on the formation of blue 1-chloro-1-nitrosocyclohexane:

$$C_6H_{10}NOH + Cl_2 = 2HCl + C_6H_{10}(Cl)NO.$$

Chlorinated urea was used as the chlorinating agent. Ogata and coworkers[21], who investigated the rearrangement of cyclohexanone oxime in sulphuric and perchloric

acids, determined the unreacted oxime in the form of the 2,4-dinitrophenylhydrazone. The analysis of oximes by their conversion into 2,4-dinitrophenylhydrazones was also done in the work by Pearson and coworkers[22]. Methods based on the isolation of the oxime or on converting it into a coloured compound are laborious and making an analysis with their use requires a relatively large quantity of oxime. These methods can be used for investigating the kinetics of relatively slow processes, since 2–3 min are needed for sampling. To obtain a kinetic curve, not less than ten points are needed and then the time for half-conversion should be ~ 10–20 min.

It is convenient to use a spectrophotometric method for the common determination of oxime and lactam in the reaction mixture. This method is based on differences in the molar absorptivities of the oxime and the lactam in solutions of sulphuric acid and oleum. At 222 nm the molar absorptivity of the oxime is considerably greater than that of the lactam. The spectrophotometric method allows the kinetics of the process to be studied at low oxime concentrations with hardly any effect on the properties of the medium (10^{-3}–10^{-4} M), and here there is no necessity to remove samples and the optical cuvette itself serves as the reaction vessel. Therefore the spectrophotometric method can be used to measure the rate of unimolecular processes which take place relatively rapidly, even those where the time for half-conversion is 30–40 s. Ultraviolet spectroscopy has been used[23-26]. Heldt[27] used a spectrophotometer for measurements in the infrared region of the spectrum to study the kinetics of the Beckmann rearrangement of the esters of oximes with *p*-toluenesulphonic acid. Thanks to this, he succeeded in determining the frequency of the absorption bands of intermediate products of the chemical process.

The Beckmann rearrangement of alicyclic ketoximes is an irreversible process. In experiments where the concentration of the oxime in the acid is low the process is first order relative to the oxime and the unimolecular constant remains unchanged right up to complete conversion of the oxime into the lactam. Tables 2–8 give the available published rate constants for the rearrangement of alicyclic ketoximes in sulphuric acid and in oleum.

The kinetics of the rearrangement of cyclohexanone oxime has been investigated in several works and these data are given in Tables 3–6. We have made experiments at low oxime concentrations[26].

Ogata and coworkers[21] studied the rearrangement of cyclohexanone oxime in relatively dilute aqueous solutions of sulphuric and perchloric acids. The sulphuric acid concentration was varied from 48.4 to 79.1% H_2SO_4 at 90° and from 89.4 to 99.6% at 60°. The perchloric acid concentration was varied within the range 47.4–59.9% $HClO_4$, at 90°. As regards the experiments in 48.4–79.1% H_2SO_4 solutions there is no doubt that under such conditions the oxime did not undergo complete hydrolysis. Since during the course of the experiments the unreacted oxime was determined the rate constants quoted[21] probably reflect the consumption of the oxime in the overall-process, including both hydrolysis and the Beckmann rearrangement. The rate constants obtained[21] for 89.4–99.6% acid cannot be doubted and are given in Table 5. Under identical conditions these constants are less than our values of the constants[26]. Pearson and coworkers[28] determined the rate constants of the Beckmann rearrangement of certain aliphatic and alicyclic ketoximes in 94.5% sulphuric acid. At the same temperature the rate constant for cyclopentanone oxime, cyclohexanone oxime,

TABLE 2. Rate constants of the Beckmann rearrangement of cyclopentanone oxime in sulphuric acid and in oleum (after Zarakhani and coworkers[25]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
91.74	70	$0.35\cdot10^{-3}$	99.85	40	$2.65\cdot10^{-3}$
	80	$0.91\cdot10^{-3}$		50	$7.71\cdot10^{-3}$
	90	$2.97\cdot10^{-3}$		60	$26.4\cdot10^{-3}$
	97	$5.64\cdot10^{-3}$		70	$78.2\cdot10^{-3}$
93.70	70	$0.48\cdot10^{-3}$		80	$21.4\cdot10^{-1}$
	80	$1.45\cdot10^{-3}$	99.91	25	$6.02\cdot10^{-3}$
	90	$3.90\cdot10^{-3}$	99.924	25	$1.00\cdot10^{-3}$
	97	$7.75\cdot10^{-3}$	99.933	25	$9.34\cdot10^{-3}$
95.42	70	$0.83\cdot10^{-3}$	99.94	25	$9.12\cdot10^{-3}$
	80	$2.48\cdot10^{-3}$	99.95	25	$1.29\cdot10^{-3}$
	80	$2.16\cdot10^{-3}$	99.986	25	$2.29\cdot10^{-3}$
	90.5	$5.94\cdot10^{-3}$	SO_3, wt. %		
	97	$12.5\cdot10^{-3}$			
97.18	70	$1.69\cdot10^{-3}$	0.1	25	$7.08\cdot10^{-3}$
	80	$4.40\cdot10^{-3}$	0.185	25	$8.51\cdot10^{-3}$
	90	$10.8\cdot10^{-3}$	0.22	25	0.10
	97.2	$22.4\cdot10^{-3}$	0.39	25	0.135
99.04	25	$2.95\cdot10^{-4}$	1.20	25	0.234
99.43	25	$5.62\cdot10^{-4}$	5.50	20	0.172
99.73	25	$1.05\cdot10^{-3}$		25	0.324
99.81	25	$2.24\cdot10^{-3}$		30	0.610
99.84	25	$3.09\cdot10^{-3}$	11.80	25	0.288
			17.20	25	0.309
			22.50	25	0.331
			27.00	25	0.308
				30	0.660
				40	1.920

TABLE 3. Rate constants of the Beckmann rearrangement of cyclohexanone oxime in sulphuric acid and in oleum (after Zarakhani and Vinnik[26]).

H_2SO_4, wt. %	T, °C	$10^3 k_{eff}$, min^{-1}	H_2SO_4, wt. %	T, °C	$10^3 k_{eff}$, min^{-1}
	97	6.01	99.50	25	0.34
82.29	90	3.57	99.73	25	0.81
	80	1.41	99.74	60	26.0
	70	0.45		50	8.84
86.03	97	11.4		40	2.76
	97	11.3	99.81	25	1.17
	90	6.44	99.842	25	1.82
	80	2.29	99.85	25	1.35
	70	0.88	99.90	25	2.57
	60	0.28	99.91	25	3.02
			99.91	25	3.38
89.94	97	21.8	99.924	25	4.26
	90	10.8	99.933	25	4.79
	80	4.9	99.936	25	4.68
	70	1.67	99.945	25	5.75
	60	0.59	99.95	25	6.16
	50	0.20	99.95	25	6.6
92.73	97	32.0	99.97	25	7.75
	90	14.95	99.986	25	15.5
	80	6.62	100.00	25	17.4
	70	2.15			
	60	0.84	SO_3, wt. %		
	50	0.30			
94.71	90	26.3			
	80	10.6	0.1	25	33.1
	70	4.14	0.185	25	34.7
	60	1.56	0.22	25	42.6
	50	0.50	0.39	25	56.2
	40	0.15	0.42	25	56.2
97 37	90	54.0	1.2	25	91.1
	80	22.0	2.22	10	16 0
	70	9.37		15.2	61.0
	60	2.88		25	108.0
	50	1.00		30	190.0
	40	0.34	7.1	10.2	18.5
98.21	90	92.0		15	35.3
	80	38.7		20	61.0
	70	15.6		25	104.0
	60	5.83		30	190.0
			15.4	10	15.5
				15	32.2
				20	56.0
				25	116.0
				30	207.0

TABLE 4. Rate constants k_{eff} of the Beckmann rearrangement of cyclohexanone oxime in oleum (after Wichterle and Roček [19]).

SO_3, wt. %	T, °C	$10^2 k_{eff}$, min^{-1}
0	30	0.04
1	30	0.69
2	30	1.08
3	30	1.68
5	30	1.92
7.5	30	2.10
10	30	1.92
12.5	30	2.10
15	30	2.72
20	30	3.80
28	30	5.50

TABLE 5. Rate constants of the Beckmann rearrangement of cyclohexanone oxime in sulphuric acid solutions at 60° (after Ogata and coworkers [21]).

H_2SO_4, wt. %	Initial oxime concentration, M	$10^2 k_{eff}$, min^{-1}
89.4	0.311	0.61
93.2	0.346	0.93
96.1	0.305	1.51
96.4	0.208	1.50
96.1	0.153	1.54
98.0	0.284	2.35
99.0	0.297	3.36
99.6	0.304	4.86

TABLE 6. Rate constants of the rearrangement of some aliphatic and alicyclic ketoximes in 94.5% sulphuric acid (after Scott and coworkers [28]).

Ketone	T, °C	$10^3 k_{eff}$, min^{-1}	Ketone	T, °C	$10^3 k_{eff}$, min^{-1}
Acetone	90 66	1.17 ± 0.01	Di-isobutyl ketone	40.43	1.47 ± 0.00
	95.82	2.10 ± 0.03		50.59	5.34 ± 0.06
	98.43	2.81 ± 0.11		60.39	17.3 ± 0.1
	107.52	7.43 ± 0.02	Cyclopentanone	51.00	1.17 ± 0.01
Diethyl ketone	50.9	1.48 ± 0.01		60.92	4.09 ± 0.04
	60.31	4.49 ± 0.07		69.90	11.8 ± 0.1
	70.47	13.9 ± 0.3	Cyclohexanone	30.0	0.557 ± 0.003
Di-isopropyl ketone	21.86	2.36 ± 0.01		40.9	2.31 ± 0.04
	30.66	7.55 ± 0.04		50.9	7.85 ± 0.12
	40.9	26.9 ± 0.1	Cycloheptanone	40.82	0.51 ± 0.01
				51.03	1.92 ± 0.06
				60.62	6.20 ± 0.1

and cycloheptanone oxime (suberone oxime) differ somewhat from the data given in Tables 2, 3, and 7. It is impossible to find the precise reason for this discrepancy. It can be assumed that the decrease in the rate constants is connected with the fact that the experiments [28] were made at relatively large concentrations of the oximes (~ 0.1 M). These results are given in Table 6. The same table also gives the rate constants for the Beckmann rearrangement of certain aliphatic ketoximes in 94.5% sulphuric acid. Although in this article the discussion of the Beckmann rearrangement of aliphatic ketoximes is being especially avoided, these figures are nevertheless of interest for a comparison of the reactivity of various ketoximes.

Wichterle and Roček [17-19] investigated the Beckmann rearrangement of cyclohexanone oxime in oleum. This rearrangement is an exothermic process, the ΔH for this reaction in the gas phase being 22 kcal $mole^{-1}$. Since the

TABLE 7. Rate constants of the Beckmann rearrangement of suberone oxime in solutions of sulphuric acid and in oleum (after Vinnik and Zarakhani [24]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
83 1	96	$3.0 \cdot 10^{-2}$	87.89	96	$5.7 \cdot 10^{-2}$
	90	$1.57 \cdot 10^{-2}$		90.2	$3.55 \cdot 10^{-2}$
85.34	96	$4.65 \cdot 10^{-2}$		90	$3.35 \cdot 10^{-2}$
	90	$2.30 \cdot 10^{-2}$		80	$1.02 \cdot 10^{-2}$
	90	$2.22 \cdot 10^{-2}$		70	$3.31 \cdot 10^{-2}$
	80	$7.62 \cdot 10^{-3}$		60	$9.50 \cdot 10^{-2}$
	70	$2.26 \cdot 10^{-3}$	93.20	90	$8.63 \cdot 10^{-2}$
90.30	96	$9.20 \cdot 10^{-2}$		80	$3.10 \cdot 10^{-2}$
	90	$5.0 \cdot 10^{-2}$		70	$1.07 \cdot 10^{-2}$
	80	$1.71 \cdot 10^{-2}$		60	$3.22 \cdot 10^{-3}$
	70	$5.90 \cdot 10^{-3}$		50	$1.04 \cdot 10^{-3}$
	60	$1.91 \cdot 10^{-3}$	97.13	90	$21.1 \cdot 10^{-2}$
95.23	90	$13.7 \cdot 10^{-2}$		80	$8.85 \cdot 10^{-2}$
	80	$5.06 \cdot 10^{-2}$		70	$3.15 \cdot 10^{-2}$
	70	$1.71 \cdot 10^{-2}$		60	$9.20 \cdot 10^{-3}$
	60	$5.50 \cdot 10^{-3}$		50	$3.36 \cdot 10^{-3}$
	50	$1.75 \cdot 10^{-3}$	99.0	25	$4.08 \cdot 10^{-4}$
99.46	25	$6.6 \cdot 10^{-4}$	99.23	25	$4.68 \cdot 10^{-4}$
99.49	25	$7.1 \cdot 10^{-4}$	99.39	70	$17.9 \cdot 10^{-2}$
99.65	25	$1.17 \cdot 10^{-3}$		60	$6.4 \cdot 10^{-2}$
99.67	80	1.15		50	$1.96 \cdot 10^{-2}$
	70	$4.04 \cdot 10^{-1}$		40	$4.77 \cdot 10^{-3}$
	60	$1.33 \cdot 10^{-1}$		40	$4.67 \cdot 10^{-3}$
	50	$3.18 \cdot 10^{-2}$		25	$8.12 \cdot 10^{-4}$
	50	$2.92 \cdot 10^{-2}$	99.77	25	$1.95 \cdot 10^{-3}$
	40	$1.09 \cdot 10^{-2}$	99.77	25	$2.04 \cdot 10^{-3}$
	40	$1.07 \cdot 10^{-2}$	99.78	25	$2.13 \cdot 10^{-3}$
	25	$1.32 \cdot 10^{-3}$	99.85	25	$3.09 \cdot 10^{-3}$
			99.86	25	$4.57 \cdot 10^{-3}$
			99.886	25	$5.37 \cdot 10^{-3}$
SO_3, wt. %			99.910	25	$5.90 \cdot 10^{-3}$
			99.927	25	$1.07 \cdot 10^{-2}$
			99.946	25	$1.17 \cdot 10^{-2}$
0.08	25	$6.32 \cdot 10^{-2}$	99.950	25	$1.51 \cdot 10^{-2}$
0.34	25	0.19	99.978	25	$2.76 \cdot 10^{-2}$
0.53	25	0.25	99.987	25	$3.39 \cdot 10^{-2}$
0.70	25	0.29	100	25	$5.0 \cdot 10^{-4}$
1.00	25	0.37			
1.36	25	0.41			
5.00	25	0.48			
6.00	25	0.48			
7.5	25	0.49			
8.2	25	0.48			
8.45	25	0.49			
8.7	25	0.51			
10.3	25	0.49			

experiments were made with a relatively high concentration of oxime (~ 0.5 M), to avoid considerable overheating caprolactam was added to the reactor in addition to the oxime. Table 4 gives the rate constants for the rearrangement which they obtained.

In carrying out the reaction in oleum the rate constant is lowered by a high concentration of the oxime and also by additions of the lactam. The following facts may be quoted as an illustration. The rate constants of the Beckmann rearrangement of cyclohexanone oxime in oleum with 0.025-0.65 wt. % SO_3 at 25° have been determined [26] at ketoxime concentrations varying from 1.7×10^{-3} M to 32.4×10^{-3} M. Such concentrations of the oxime are almost without effect on the rate constant. These results are shown in Table 9. In the same table are given the rate constants for oleum with 1% SO_3, obtained by Wichterle and Roček [18].

In their experiments [18], the oxime concentration was ~ 0.5 M and together with this additions of caprolactam were made (14 g per 15 g oleum). This constant, even at 30°, is much less than the constant at 25° obtained with low oxime concentrations. This shows that additions of large amounts of oxime and lactam significantly lower the catalytic activity of oleum. As already mentioned above, low rate constants are also obtained in aqueous solutions of sulphuric acid in working with relatively large amounts of

TABLE 8. Rate constants of the Beckmann rearrangement of cyclododecanone oxime in sulphuric acid and in oleum (after Vinnik and Zarakhani[23]).

H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}	H_2SO_4, wt. %	T, °C	k_{eff}, min^{-1}
88.07	87.7	$6.2 \cdot 10^{-2}$	90.33	87.7	$9.10 \cdot 10^{-2}$
	78.6	$2.48 \cdot 10^{-2}$		78.6	$3.77 \cdot 10^{-2}$
	68.7	$8.41 \cdot 10^{-3}$		68.7	$1.31 \cdot 10^{-2}$
	58.9	$2.57 \cdot 10^{-3}$		58.9	$4.15 \cdot 10^{-3}$
	49.3	$7.85 \cdot 10^{-4}$		49.3	$1.21 \cdot 10^{-3}$
93.29	87.7	$1.58 \cdot 10^{-1}$	95.67	87.7	$2.52 \cdot 10^{-1}$
	87.7	$1.35 \cdot 10^{-1}$		78.6	$1.04 \cdot 10^{-1}$
	78.6	$6.9 \cdot 10^{-2}$		68.7	$3.89 \cdot 10^{-2}$
	68.7	$2.48 \cdot 10^{-2}$		58.9	$1.35 \cdot 10^{-2}$
	58.9	$7.75 \cdot 10^{-3}$		49.3	$3.43 \cdot 10^{-3}$
	49.3	$2.51 \cdot 10^{-3}$	99.85	25	$8.32 \cdot 10^{-3}$
97.67	78.6	$1.88 \cdot 10^{-1}$	99.856	25	$1.07 \cdot 10^{-2}$
	68.7	$7.05 \cdot 10^{-2}$	99.86	25	$1.23 \cdot 10^{-2}$
	58.9	$2.71 \cdot 10^{-2}$	99.886	25	$1.44 \cdot 10^{-2}$
	49.3	$8.67 \cdot 10^{-3}$	99.918	25	$2.24 \cdot 10^{-2}$
99.20	25	$1.02 \cdot 10^{-2}$	99.927	25	$2.89 \cdot 10^{-2}$
99.23	25	$1.26 \cdot 10^{-2}$	99.946	25	$3.16 \cdot 10^{-2}$
99.46	25	$1.91 \cdot 10^{-2}$	99.954	25	$4.47 \cdot 10^{-2}$
99.65	25	$3.1 \cdot 10^{-2}$	99.987	25	$7.95 \cdot 10^{-2}$
99.77	25	$5.25 \cdot 10^{-2}$	100.0	25	$1.26 \cdot 10^{-1}$
99.78	25	$5.89 \cdot 10^{-2}$			
99.79	25	$7.95 \cdot 10^{-2}$	SO_3, wt. %		
SO_3, wt. %			0.08	25	$1.91 \cdot 10^{-1}$
			0.34	25	$0.51 \cdot 10^{-1}$
1.38	24.9	1.16	0.53	25	0.69
	24.9	1.14	0.7	25	0.89
	20.0	0.64	1	25	0.98
	15	0.35	1.36	25	1.12
	10	0.18	3.86	25	1.57
11.4	25	1.51		25	1.57
	20	0.85		20	0.85
	15	0.45		15	0.44
	10	0.24		10	0.28
33	25	1.67			
	20	0.91			
	15	0.47			
	10	0.23			

TABLE 9. Effect of additions of the oxime and the lactam on the rate constant of the Beckmann rearrangement of cyclohexanone oxime in oleum.

T, °C	SO_3, wt. %	Cyclohexanone concn. $\times 10^3$, M	k_{eff}, min^{-1}	T, °C	SO_3, wt. %	Cyclohexanone concn. $\times 10^3$, M	k_{eff}, min^{-1}
		1.01	0.810			2.06	0.546
		1.51	0.810			3.04	0.585
		2.82	0.770	25	0.40	4.73	0.540
		2.83	0.753			13.5	0.535
25	0.65	3.69	0.695			19.7	0.558
		3.79	0.690			2.3	0.364
		7.51	0.604	25	0.17	7.35	0.334
		8.15	0.702			26.0	0.345
		12.7	0.615			1.73	0.215
		16.7	0.712			2.16	0.222
				25	0.025	30.3	0.184
						32.4	0.188
				30	1.0		$0.69 \cdot 10^{-2}$

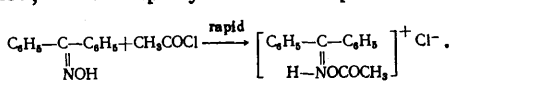
oxime (0.15–0.35 M). This should be taken into account in investigations where the rate constants are determined to provide information about the reactivity of substances of different chemical structure.

V. MECHANISM OF THE BECKMANN REARRANGEMENT OF OXIMES

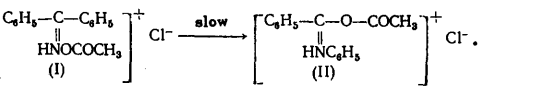
Until recently information on the mechanism of the Beckmann rearrangement of oximes was based on investigations of a preparative nature. Despite the fact that such investigations did not concern alicyclic ketoximes, it is helpful to analyse them, since it would be expected that in some of these conditions the rearrangement mechanism will not differ significantly for different ketoximes.

Sluiter[29] considered that not the oximes as such, but their esters, undergo the rearrangement. The exquisite preparative procedures of Kuhara[30] are based on this hypothesis.

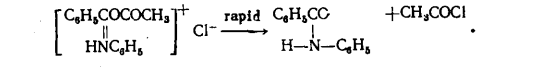
In studying the action of acid chlorides on the Beckmann rearrangement of benzophenone oxime, Kuhara observed that the ester of benzophenone and benzenesulphonic acid is rearranged at a very high rate. Under these conditions the chloroacetate exhibits much less reactivity and the acetate hardly undergoes any rearrangement. Benzophenone oximium acetate undergoes rearrangement on the addition of hydrogen chloride. Kuhara proposed the following mechanism. In the presence of HCl, acyl chlorides are obtained, which rapidly form a complex with the oxime:



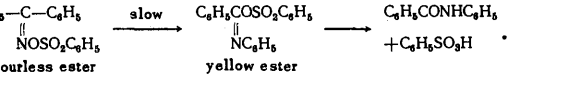
The isomerisation of this complex is the limiting stage:



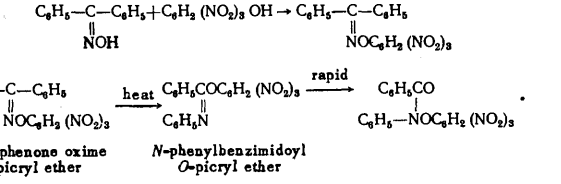
Complex (II) is an addition product of acetyl chloride and benzanilide. It decomposes rapidly with formation of benzanilide:



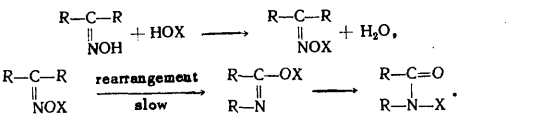
Kuhara showed that the benzenesulphonate which is formed in the reaction of benzenesulphonyl chloride with the sodium salt of benzophenone oxime is colourless. In time, this ester isomerises into another ester, which is yellow. In the presence of moisture (in moist air) the yellow ester is converted into benzanilide:



Chapman[31–34] obtained similar results for the Beckmann rearrangement of benzophenone oxime under the action of picric acid. The oxime and the acid form benzophenone oxime *O*-picryl ether which isomerises on heating into *N*-phenylbenzimidoyl *O*-picryl ether; the latter is rapidly converted into a salt of an anilide.



Chapman considers[31] that the formation of ethers can be explained by the catalytic action of many substances on the process of the Beckmann rearrangement of oximes. In the general example the mechanism can be represented by the following scheme:



According to Chapman, the chlorides and oxide chlorides of phosphorus and sulphur, aryl sulphonyl chlorides, and, probably, sulphuric acid also act in this way. On carrying out the rearrangement under the action of hydrogen chloride in dichloroethane solution, the kinetic curves for the process have an autocatalytic nature[31]. The action of hydrogen chloride cannot be explained by the mechanism given above. This is also shown by the results of Stieglitz and Peterson[35,36], who showed that *N*-chloro-compounds of the type R–C–R do not undergo the Beckmann rearrangement.
‖
NCl

Pearson and Ball[37] consider that the mechanism for the Beckmann rearrangement proposed by Kuhara and Chapman explains the catalytic action of sulphuric acid in this process.

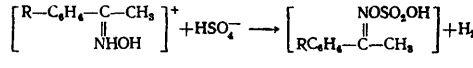
Firstly the oxime and acid form a salt-like complex. This stage is exothermic and in aqueous solutions of the acid it is reversible.

Stage I:



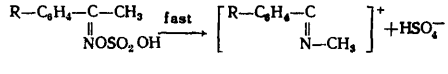
Then the salt-like complex loses water with the formation of the sulphate.

Stage II:



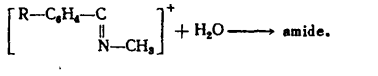
Unlike Chapman, Pearson and Ball assume that the dehydration stage, as a result of which sulphate is formed, is the slowest in the process. The sulphate is rapidly rearranged into a dehydrated ionised form of the amide (stage IIIa).

Stage IIIa:



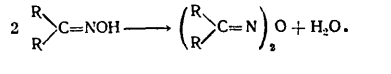
In aqueous solutions the ionised form of the amide rapidly adds on water (stage IIIb).

Stage IIIb:

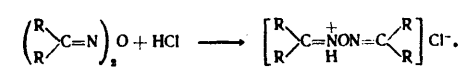


Dehydration of the oxime during the course of the Beckmann rearrangement has been demonstrated in experiments of Brodskii and Miklukhin[38,39]. They carried out the Beckmann rearrangement of benzophenone oxime in ethereal solution under the catalytic action of phosphorus pentachloride at 15°. After the process had ended, the reaction mixture was diluted with water containing an excess of ^{18}O. In the benzanilide obtained, the ^{18}O content was the same as in the water used for the saponification. In acid and neutral media benzanilide does not exchange this oxygen.

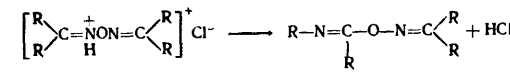
Stephen and Staskun[40] proposed another mechanism for the Beckmann rearrangement of ketoximes. In the opinion of these authors, the ketoximes form anhydrides:



Hydrogen chloride adds on to the molecule of the anhydride and forms a salt:

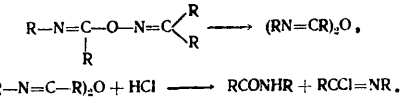


In the salt, according to the authors[40], the symmetry of the anhydride is destroyed, thanks to which it is rearranged into a ketoximimidate:



ketoximimidate

This rearranges into the imidoyl anhydride, which in the presence of HCl is converted into an amide:



This mechanism was proposed to explain the catalytic action of aprotic acids. According to this mechanism the reactive form is formed from the anhydride of the ketoxime. When the conditions are such that the fraction of the oxime present as anhydride is small, the process will be second order in relation to the oxime.

There are still no facts to confirm this conclusion. The authors of this scheme assume that the proton is attached to one of the nitrogen atoms. The possibility of attachment of the proton to the oxygen atom is not excluded.

We will analyse the kinetic demonstrations of the mechanism of the limiting stage of the Beckmann rearrangement of alicyclic ketoximes in sulphuric acid. As shown above, in aqueous solutions of sulphuric acid oximes are found in three forms: the un-ionised form RNOH, the protonated form $RNOH_2^+$, and the ion pairs $RNOH_2^+.HSO_4^-$. It is evident that no one of these forms in isolation is capable of reaction in the Beckmann rearrangement. The un-ionised form is not reactive since this process does not take place without a catalyst. The protonated form is also incapable of reaction in this process, since in solutions of the acid where almost all the oxime is present in this form the rate of the process rises on increasing the acidity of the medium. Under conditions where the rate constant of the Beckmann rearrangement rises the concentration of the ion pairs falls; in solutions with $>99\%$ H_2SO_4 the fraction of ion pairs calculated on the total oxime concentration can be neglected. Consequently, the ion pairs $RNOH_2^+.HSO_4^-$ are not reactive in this process.

In dilute oleum with increase in the SO_3 concentration in the solution the rate constant of the Beckmann rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime rises to a certain value and then remains constant on further increase of the oleum concentration (Fig. 4).

For unimolecular processes the value of the rate constant is often reached under conditions where all the reagent is present in a reactive form. This form can be either a complex of the reagent with the catalyst or an ionised form produced by interaction of the reagent with the solution containing the catalyst. The ratio of the observed rate constant to the limiting value of the rate constant expresses the ratio of the concentration of the reactive species to the total concentration of the reagent under the given conditions.

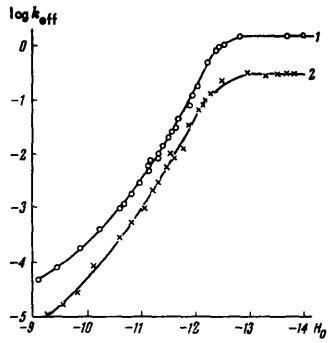


Fig. 4. Variation of log k_{eff} with H_0 in the Beckmann rearrangement of cyclopentanone oxime (2) and cyclododecanone oxime (1) in sulphuric acid and in oleum at 25°.

Judging from this criterion, in aqueous solutions of sulphuric acid right up to 100% H_2SO_4 the fraction of reactive species is low in comparison with the oxime concentration. This makes it possible to find the mechanism of formation of the reactive species from the dependence of the observed rate constants on the thermodynamic activities of the acid and water, and also the acidity of the acid solutions. In this it is understood that the kinetic experiments were made with the same low concentrations of oxime so that their effect on the values of the parameters mentioned could be neglected. The activity of the acid and water and the acidity functions for the range we are interested in are known for 25°. To be able to compare the values of k_{eff} with the quantities mentioned over wide ranges at 25° for relatively dilute solutions the rate constants were extrapolated from higher temperatures. Tables 10–13 give the values of k_{eff} at 25° for cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime

TABLE 10. Rate constants of the Beckmann rearrangement of cyclopentanone oxime at 25°*.

H_2SO_4, wt. %	log k_{eff}, min^{-1}	log a_{H_2O}	H_0	log $a_{H_2SO_4}$	log $k_{eff}a_{H_2O}$	$\log\frac{a_{H_2O}h_0}{a_{H_2SO_4}}k_{eff}$
91.74	—4.98	—3.92	—9.24	9.07	—8.90	
93.70	—4.76	—4.26	—9.54	9.20	—9.02	
95.42	—4.55	—4.55	—9.81	9.32	—9.10	
97.18	—4.05	—5.00	—10.10	9.41	—9.05	
99.04	—3.53	—5.85	—10.58	9.50	—9.38	—8.30
99.43	—3.25	—6.21	—10.79	9.51	—9.46	—8.18
99.73	—2.98	—6.82	—11.06	9.52	—9.80	—8.26
99.81	—2.65	—7.10	—11.19	9.52	—9.75	—8.08
99.842	—2.51	—7.26	—11.27	9.53	—9.77	—8.03
99.85	—2.45	—7.30	—11.28	9.53	—9.75	—8.10
99.91	—2.22	—7.70	—11.46	9.53	—9.92	—7.99
99.924	—2.00	—7.82	—11.53	9.53	—9.82	—7.82
99.933	—2.03	—7.90	—11.56	9.53	—9.93	—7.90
99.94	—2.04	—7.97	—11.60	9.53	—10.01	—7.94
99.95	—1.89	—8.12	—11.64	9.53	—10.01	—7.87
99.986	—1.44	—8.86	—11.85	9.53	—10.30	—7.98
SO_3, wt. %						
0.1	—1.15	—9.58	—12.05	9.53	—10.73	—8.21
0.185	—1.07	—9.77	—12.12	9.53	—10.84	—8.25
0.22	—1.00	—9.83	—12.15	9.53	—10.83	—8.20
0.39	—0.87	—10.10	—12.25	9.53	—10.97	—8.25
1.2	—0.63	—10.67	—12.47	9.52	—11.30	—8.35

* The activity of the acid $a_{H_2SO_4}$ is taken from Giauque and coworkers [8], the activity of water from Giauque and coworkers [8] and Vinnik and Ryabova [10], and H_0 from Ryabova and coworkers [9].

TABLE 11. Rate constants of the Beckmann rearrangement of cyclohexanone oxime at 25°.

H_2SO_4, wt. %	log k_{eff}	log a_{H_2O}	H_0	log $a_{H_2SO_4}$	log $k_{eff}a_{H_2O}$	$\log\frac{a_{H_2O}h_0}{a_{H_2SO_4}}k_{eff}$
82.29	—4.74	—2.55	—7.88	+7.99	—7.29	—7.40
86.03	—4.38	—3.07	—8.45	8.50	—7.45	—7.50
89.94	—4.05	—3.63	—9.02	8.92	—7.68	—7.58
92.73	—3.86	—4.09	—9.42	9.14	—7.95	—7.67
94.71	—3.59	—4.42	—9.69	9.27	—8.01	—7.59
97.37	—3.28	—5.06	—10.13	9.41	—8.34	—7.62
98.21	—2.96	—5.38	—10.32	9.46	—8.34	—7.48
99.50	—2.47	—6.31	—10.84	9.51	—8.78	—7.45
99.73	—2.09	—6.82	—11.05	9.52	—8.91	—7.38
99.74	—2.36	—6.85	—11.08	9.52	—9.21	—7.65
99.81	—1.93	—7.10	—11.19	9.52	—9.03	—7.36
99.842	—1.74	—7.26	—11.26	9.53	—9.00	—7.27
99.85	—1.87	—7.29	—11.28	9.53	—9.16	—7.41
99.90	—1.59	—7.61	—11.43	9.53	—9.20	—7.30
99.91	—1.52	—7.70	—11.46	9.53	—9.22	—7.29
99.91	—1.47	—7.70	—11.46	9.53	—9.17	—7.24
99.924	—1.37	—7.82	—11.51	9.53	—9.19	—7.21
99.933	—1.32	—7.90	—11.55	9.53	—9.22	—7.20
99.936	—1.33	—7.97	—11.57	9.53	—9.30	—7.26
99.945	—1.24	—8.00	—11.61	9.53	—9.24	—7.16
99.95	—1.21	—8.12	—11.64	9.53	—9.33	—7.22
99.95	—1.18	—8.12	—11.64	9.53	—9.30	—7.19
99.97	—1.11	—8.50	—11.74	9.53	—9.61	—7.40
99.986	—0.81	—8.88	—11.84	9.53	—9.69	—7.38
100	—0.76	—9.09	—11.94	9.53	—9.84	—7.43
SO_3, wt. %						
0.1	—0.48	—9.58	—12.06	9.53	—10.06	—7.51
0.185	—0.46	—9.77	—12.13	9.53	—10.23	—7.61
0.22	—0.37	—9.83	—12.16	9.53	—10.20	—7.55
0.39	—0.25	—10.10	—12.26	9.53	—10.35	—7.60
0.42	—0.25	—10.14	—12.27	9.53	—10.39	—7.63
1.2	—0.04	—	—	—	—	—
2.22	+0.03	—	—	—	—	—
7.1	+0.02	—	—	—	—	—
15.4	+0.06	—	—	—	—	—

TABLE 12. Rate constants of the Beckmann rearrangement of suberone oxime at 25°.

H_2SO_4, wt. %	log k_{eff}, min^{-1}	H_0	log $a_{H_2SO_4}$	log a_{H_2O}	log $k_{eff}a_{H_2O}$	$\log\frac{a_{H_2O}h_0}{a_{H_2SO_4}}k_{eff}$
85.34	—5.48	—8.34	8.42	—2.98	—8.46	—
87.89	—5.21	—8.73	8.72	—3.33	—8.54	
90.30	—4.76	—9.07	8.96	—3.69	—8.45	
93.20	—4.45	—9.48	9.17	—4.16	—8.61	
95.23	—4.23	—9.76	9.30	—4.52	—8.75	
97.13	—3.9	—10.08	9.41	—4.99	—8.89	
98.05	—3.7	—10.28	9.45	—5.31	—9.01	
99.23	—3.33	—10.68	9.50	—5.98	—9.31	—8.13
99.39	—3.09	—10.76	9.51	—6.16	—9.25	—8.00
99.46	—3.18	—10.81	9.51	—6.25	—9.43	—8.13
99.49	—3.15	—10.83	9.51	—6.30	—9.45	—8.13
99.65	—2.93	—10.96	9.52	—6.58	—9.51	—8.07
99.67	—2.88	—10.98	9.52	—6.65	—9.53	—8.07
99.77	—2.71	—11.11	9.52	—6.95	—9.66	—8.07
99.77	—2.69	—11.11	9.52	—6.95	—9.64	—8.05
99.78	—2.67	—11.13	9.52	—6.98	—9.65	—8.04
99.85	—2.51	—11.28	9.52	—7.30	—9.81	—8.05
99.86	—2.34	—11.31	9.53	—7.35	—9.69	—7.91
99.886	—2.27	—11.39	9.53	—7.50	—9.77	—7.91
99.910	—2.23	—11.47	9.53	—7.69	—9.92	—7.98
99.918	—2.08	—11.50	9.53	—7.78	—9.86	—7.89
99.927	—1.97	—11.53	9.53	—7.88	—9.85	—7.85
99.946	—1.93	—11.62	9.53	—8.08	—10.01	—7.92
99.960	—1.82	—11.70	9.53	—8.28	—10 10	—7.93
99.978	—1.56	—11.83	9.53	—8.67	—10.23	—7.87
99.987	—1.47	—11.89	9.53	—8.86	—10.33	—7.97
100	—1.30	—11.95	9.53	—9.09	—10 39	—7.97
SO_3, wt. %						
0.08	—1.2	—12.05	9.53	—9.38	—10.58	—8.06
0.34	—0.72	—12.23	9.53	—10.03	—10.75	—8.05
0.53	—0.60	—12 32	9.53	—10.26	—10.86	—8.07
0.7	—0.52	—12.37	9.52	—10.40	—10.92	—8.07
1	—0.42	—12.44	9.52	—10.50	—10.92	—8.00
1.36	—0 39	—12.51	9.52	—10.64	—11.03	—8.04

TABLE 13. Rate constants of the Beckmann rearrangement of cyclododecanone oxime at 25°.

H_2SO_4, wt. %	$\log k_{eff}$	H_0	$\log a_{H_2SO_4}$	$\log a_{H_2O}$	$\log k_{eff}a_{H_2O}$	$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}} k_{eff}$
90.36	−4.32	− 9.10	8.96	−3.69	−8.01	
93.34	−4.04	− 9.45	9.18	−4.19	−8.23	
95.70	−3.72	− 9.85	9.33	−4.62	−8.34	
97.70	−3.36	−10.20	9.44	−5.17	−8.53	
99.20	−2.99	−10.61	9.50	−5.95	−8.94	
99.23	−2.50	−10.68	9.50	−5.98	−8.88	
99.46	−2.72	−10.81	9.51	−6.25	−8.97	−7.67
99.65	−2.51	−10.96	9.52	−6.58	−9.09	−7.65
99.77	−2.28	−11.12	9.52	−6.95	−9.23	−7.69
99.78	−2.23	−11.14	9.52	−6.98	−9.21	−7.59
99.79	−2.1	−11.15	9.52	−7.02	−9.12	−7.49
99.85	−2.08	−11.28	9.52	−7.30	−9.38	−7.62
99.856	−1.97	−11.30	9.53	−7.33	−9.30	−7.53
99.86	−1.91	−11.31	9.53	−7.35	−9.26	−7.48
99.886	−1.84	−11 38	9.53	−7.50	−9.34	−7.49
99.918	−1.65	−11.50	9.53	−7.78	−9.43	−7.46
99.927	−1.54	−11.55	9.53	−7.88	−9.42	−7.40
99.946	−1.50	−11.63	9.53	−8.08	−9.58	−7.48
99.954	−1.35	−11.68	9.53	−8.20	−9.55	−7.40
99.987	−1.1	−11.87	9.53	−8.86	−9.96	−7.62
100.0	−0.9	−11.94	9.53	−9.09	−9.99	−7.58
SO_3, wt. %						
0.08	−0.72	−12.03	9.53	− 9.38	−10.10	−7.59
0.34	−0.29	−12.23	9.53	−10.03	−10.32	−7.62
0.53	−0.16	−12.31	9.53	−10.26	−10.42	−7.64
0.7	−0.05	−12.38	9.52	−10.40	−10.45	−7.59
1	−0.01	−12.43	9.52	−10.50	−10.51	−7.60
1.36	+0.05	−12.51	9.52	−10.64	−10.63	−7.64
3.86	+0.20					
11.4	+0.20					
33	+0.22					

from published sources[23-26]. In these tables values of H_0, a_{H_2O}, $a_{H_2SO_4}$, and values of $\log k_{eff}a_{H_2O}$ are given for corresponding concentrations of acid and oleum.

As these tables show, $\log k_{eff}a_{H_2O}$ remains constant in the range 91.74–97.18% H_2SO_4 for cyclopentanone oxime and in 85.34–90.3% acid for suberone oxime. Such a dependence can be obtained if two conditions are fulfilled: (a) the reactive form is produced in the dehydration of either $RNOH_2^+$ ions or the species $RNOH_2^+.HSO_4^-$; (b) almost all the oxime in the solution is present in a form which is dehydrated. On the basis of the above considerations the oxime can be present in such solutions as the ion pairs $RNOH_2^+.HSO_4^-$ and the protonated species $RNOH_2^+$. Dehydration of the ion pairs (salt) can be represented by Eqn. (1):

$$RNOH_2^+ \cdot HSO_4^- \rightleftarrows RN^+ \cdot HSO_4^- + H_2O. \quad (1)$$

Dehydration of the protonated species can be expressed by Eqn. (2):

$$RNOH_2^+ \rightleftarrows RN^+ + H_2O. \quad (2)$$

The ion pairs $RN^+.HSO_4^-$ can be considered as an association product of the dehydrated ions RN^+ with the HSO_4^- anions:

$$RN^+ + HSO_4^- \rightleftarrows RN^+HSO_4^-. \quad (3)$$

We will derive an equation for the variation of the observed rate constants k_{eff} on the quantities a_{H_2O}, $a_{H_2SO_4}$, and h_0 for instances when either the ions RN^+ or the ion pairs $RN^+.HSO_4^-$ are capable of reaction. We will use K_c to denote the thermodynamic constant of salt formation:

$$RNOH_2^+ + HSO_4^- \rightleftarrows RNOH_2^+ \cdot HSO_4^-,$$

$$K_c = \frac{a_{RNOH_2^+} \, a_{HSO_4^-}}{a_{(RNOH_2^+ \cdot HSO_4^-)}}, \quad (4)$$

where $a_{RNOH_2^+}$, $a_{(RNOH_2^+.HSO_4^-)}$, and $a_{HSO_4^-}$ are the activities of of the $RNOH_2^+$ cations, the $RNOH_2^+.HSO_4^-$ species, and the HSO_4^- anions. We will draw up the balance equation for the oxime under conditions when the concentration of the reactive species (this can be either the RN^+ ions or the $RNOH_2^+.HSO_4^-$ ion pairs) can be neglected. Such a condition is observed in the Beckmann rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime in sulphuric acid solutions up to 100% H_2SO_4.

$$C_0 = C_{RNOH} + C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-},$$

where C_0 is the total concentration of the oxime.

As already mentioned, alicyclic oximes have a high basicity. In solutions of acids where the Beckmann rearrangement occurs the relative concentrations of the un-ionised species of the oxime can be neglected:

$$C_{RNOH} \ll C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-},$$

$$C_0 = C_{RNOH_2^+} + C_{RNOH_2^+ \cdot HSO_4^-}. \quad (5)$$

We will express $C_{RNOH_2^+}$ and $C_{RNOH_2^+.HSO_4^-}$ in terms of C_0 and the equilibrium constant K_c:

$$C_{RNOH_2^+} = \frac{C_0}{1 + \frac{a_{HSO_4^-}}{K_c} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+ \cdot HSO_4^-)}}}, \quad (6)$$

$$C_{RNOH_2^+ \cdot HSO_4^-} = \frac{C_0}{1 + \frac{K_c}{a_{HSO_4^-}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RNOH_2^+}}}. \quad (7)$$

The activity of the anions of the acid $a_{HSO_4^-}$ is conveniently expressed in terms of $a_{H_2SO_4}$ and h_0:

$$a_{H_2SO_4} = K_{2A} \cdot a_{H^+} \cdot a_{HSO_4^-},$$

where K_{2A} is the thermodynamic constant for the dissociation of the hydrogen sulphate ions:

$$HSO_4^- \rightleftarrows SO_4^{2-} + H^+.$$

At 25°,[41] $K_{2A} = 1.2 \times 10^{-2}$. Since in aqueous solutions of strong acids[42], $a_{H^+} = h_0$,

$$a_{H_2SO_4} = K_{2A} \cdot h_0 \cdot a_{HSO_4^-}; \quad a_{HSO_4^-} = \frac{a_{H_2SO_4}}{K_{2A} \cdot h_0}.$$

We will use K_2 and K_3 to denote the expressions in the activities of the equilibrium constants of the processes of dehydration (1) and (2):

$$K_2 = \frac{a_{(RNOH_2^+ \cdot HSO_4^-)}}{a_{RN^+ \cdot HSO_4^-} \cdot a_{H_2O}}; \quad K_3 = \frac{a_{RNOH_2^+}}{a_{RN^+} \cdot a_{H_2O}}.$$

We will express the concentrations of the $RN^+.HSO_4^-$ species and RN^+ ions in terms of C_0, the equilibrium constants, and the quantities a_{H_2O}, h_0, and $a_{H_2SO_4}$:

$$C_{RN^+} = \frac{C_0 \frac{f_{RNOH_2^+}}{K_3 \cdot f_{RN^+}} \cdot \frac{1}{a_{H_2O}}}{1 + \frac{a_{H_2SO_4}}{K_{2A} \cdot K_c \cdot h_0} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+ \cdot HSO_4^-)}}}, \quad (8)$$

$$C_{RN^+ \cdot HSO_4^-} = \frac{C_0 \cdot \frac{1}{K_2 \cdot a_{H_2O}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RN^+ \cdot HSO_4^-}}}{1 + \frac{K_{2A} \cdot K_c \cdot h_0}{a_{H_2SO_4}} \cdot \frac{f_{(RNOH_2^+ \cdot HSO_4^-)}}{f_{RNOH_2^+}}}, \quad (9)$$

where $f_{RNOH_2^+}$, f_{RN^+}, $f_{RNOH_2^+.HSO_4^-}$, and $f_{RN^+.HSO_4^-}$ are the activity coefficients of the ions $RNOH_2^+$ RN^+, and the ion pairs $RNOH_2^+.HSO_4^-$ and $RN^+.HSO_4^-$ respectively.

It is assumed that the rate of the limiting stage is determined by the concentration of the dehydrated species. Therefore with change in the properties of the medium k_{eff} should change by the same equation as the concentration of the reactive species. We will analyse Eqns. (8) and (9). The analysis of these is most convenient with the example of suberone oxime, since it is reliably known that in 99% sulphuric acid it is present completely in the form of the protonated species $RNOH_2^+$. Consequently, for such solutions in Eqn. (8):

$$1 \gg \frac{a_{HSO_4^-}}{K_c} \cdot \frac{f_{RNOH_2^+}}{f_{(RNOH_2^+.HSO_4^-)}}$$

and

$$C_{RN^+} = \frac{C_0}{a_{H_2O}} \cdot \frac{f_{RNOH_2^+}}{K_3 \cdot f_{RN^+}}.$$

It is well known how the ratio of the activity coefficients $f_{RNOH_2^+}/f_{RN^+}$ changes with the sulphuric acid concentration. Since, in the present example we are considering the very narrow range from 99 to 100% H_2SO_4, where it is possible to neglect the relative concentration of the reactive species it can be assumed that $f_{RNOH_2^+}/f_{RN^+}$ is constant. Then

$$\frac{C_{RN^+}}{C_0} = \frac{\text{const}}{K_3 \cdot a_{H_2O}}.$$

If the dehydrated ion RN^+ is reactive, then in the range 99–100% H_2SO_4 for the effective rate constant the equation

$$k_{eff} a_{H_2O} = \text{const} \frac{k_{true}}{K_1}$$

should hold, where k_{true} is the true rate constant.

As Table 12 shows, the quantity $\log k_{eff} a_{H_2O}$ for suberone oxime is not constant in 99.23–100% H_2SO_4. In this range the quantity $\log k_{eff} a_{H_2O}$ falls by a factor of 12. This greatly exceeds the possible change in the ratio $f_{RNOH_2^+}/f_{RN^+}$ in this narrow range.

The quantity $\log k_{eff} a_{H_2O}$ is also not constant in such a narrow range for other oximes (see Tables 10, 11, and 13). Consequently, the limiting stage of the Beckmann rearrangement of alicyclic ketoximes is not the isomerisation of the dehydrated ions RN^+. Since in the sulphuric acid concentration range being considered suberone oxime is almost completely present as the ions $RNOH_2^+$, in Eqn. (9):

$$1 \ll K_{2A} \cdot K_c \cdot \frac{h_0}{a_{H_2SO_4}} \cdot \frac{f_{(RNOH_2^+.HSO_4^-)}}{f_{RNOH_2^+}}$$

$$C_{RN^+.HSO_4^-} = \frac{C_0 \cdot a_{H_2SO_4} \cdot f_{RNOH_2^+}}{a_{H_2O} \cdot h_0 \cdot K_{2A} \cdot K_2 K_c \cdot f_{RN^+.HSO_4^-}}, \quad (10)$$

and in the present instance it can be taken that in the narrow range 99–100% H_2SO_4 the ratio of activity coefficients $f_{RNOH_2^+}/f_{RN^+.HSO_4^-}$ will be almost constant, and

$$\frac{C_{RN^+.HSO_4^-}}{C_0} = \frac{\text{const}}{K_{2A} \cdot K_2 \cdot K_c} \cdot \frac{a_{H_2SO_4}}{a_{H_2O} \cdot h_0}.$$

In the range considered the concentration of the reactive species can be neglected. If the ion pairs $RN^+.HSO_4^-$ are reactive, then:

$$k_{eff} = k_{true} \frac{a_{H_2SO_4}}{a_{H_2O} \cdot h_0} \cdot \frac{\text{const}}{K_{2A} \cdot K_2 \cdot K_c}.$$

In this instance the product $k_{eff} a_{H_2O} h_0 / a_{H_2SO_4}$ will be constant.

On increasing the acid concentration from 99.23 to 100% H_2SO_4 the effective rate constant of the Beckmann rearrangement of suberone oxime rises by a factor of 108. As the results in Table 12 show, in this interval the quantity $k_{eff} a_{H_2O} h_0 / a_{H_2SO_4}$ is almost constant. The scatter which occurs $\left(\log \frac{k_{eff} a_{H_2O} h_0}{a_{H_2SO_4}} = -8 \pm 0.1\right)$ is evidently connected with the error in determining the effective rate constants, the activity of water, the acidity h_0, and also with possible small changes in the ratio $f_{RNOH_2^+}/f_{RN^+.HSO_4^-}$. This quantity is also almost constant in this range for other oximes (see Tables 10, 11, and 13). This suggests the conclusion that the dehydrated ion pairs in this process are reactive. To obtain the complete equation for the dependence of k_{eff} on a_{H_2O}, h_0, and $a_{H_2SO_4}$ it is necessary to add to the balance equation derived above the concentration of the reactive species $RN^+.HSO_4^-$:

$$C_0 = C_{RNOH_2^+} + C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-}.$$

If the $RNOH_2^+$ and $RNOH_2^+.HSO_4^-$ concentrations are expressed in terms of the concentration of the reactive species $RN^+.HSO_4^-$ and the equilibrium constants, we obtain:

$$C_{RN^+.HSO_4^-} = \frac{C_0}{1 + \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} \cdot K_{2A} \cdot K_2 \cdot K_c \cdot \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+}} + K_2 \cdot a_{H_2O} \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+.HSO_4^-}}}.$$

Precise analysis of this equation is difficult, since it is unknown how the activity coefficients in this equation change. There are grounds for assuming that with change in the sulphuric acid concentration over a wide interval (for example, from 85 to 100% acid) the activity coefficients of the ions and species mentioned change considerably. In the present instance the equation includes the ratios

$$\frac{f_{RN^+.HSO_4^-}}{f_{(RNOH_2^+.HSO_4^-)}} \text{ and } \frac{f_{RN^+.HSO_4^-}}{f_{RNOH_2^+}}.$$

There is reason to think that the ratio of the activity coefficients of two ion pairs will depend weakly on the acid concentration. As already mentioned above, in relatively dilute sulphuric acid solutions, where the Beckmann transformation occurs, the relation $\log k_{eff} a_{H_2O} = \text{const}$ is obeyed. Such a relation can be kept if the ion pairs $RN^+.HSO_4^-$ are reactive and the ratio $f_{RN^+.HSO_4^-}/f_{RNOH_2^+}$ is independent of the acid concentration. We assume that this ratio is constant also in more concentrated solutions of the acid.

We will represent $K_{2A} K_2 K_c f_{RN^+.HSO_4^-}/f_{RNOH_2^+}$ by $K_2' K_c'$ and $K_2 f_{RN^+.HSO_4^-}/f_{RNOH_2^+.HSO_4^-}$ by K_2'. Then:

$$C_{RN^+.HSO_4^-} = \frac{C_0}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}. \quad (11)$$

We will write the expression for W, the rate constant of the process:

$$W = k \frac{a^*}{f^*} = k \frac{a_{RN^+.HSO_4^-}}{f^*} = k \frac{C_{RN^+.HSO_4^-} \cdot f_{RN^+.HSO_4^-}}{f^*},$$

where a^* and f^* are the activity and activity coefficient of the activated complex. The activated state is formed from the ion pairs $RN^+.HSO_4^-$. The activated complex and the ion pairs $RO^+.HSO_4^-$ have the same composition; therefore we

will assume that the ratio $f_{RN^+.HSO_4^-}/f^*$ is independent of the composition of the reaction medium:

$$W = k_{true} \cdot C_{RN^+.HSO_4^-} = \frac{k_{true}\, C_0}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}$$

$$\frac{W}{C_0} = k_{eff} = \frac{k_{true}}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}, \qquad (12)$$

Eqn. (12) describes the variation of the effective rate constant k_{eff} of the Beckmann rearrangement of aliphatic ketoximes on the quantities a_{H_2O}, h_0, and $a_{H_2SO_4}$ of aqueous solutions of sulphuric acid and oleum. In solutions where $C_{RN^+.HSO_4^-} + C_{RNOH_2^+} \ll C_{RNOH_2^+.HSO_4^-}$ the following relation should hold:

$$k_{eff} \cdot a_{H_2O} = \frac{k_{true}}{K_2'}.$$

As already mentioned, such a dependence exists for suberone oxime and cyclopentanone oxime. It is not valid for cyclohexanone oxime and cyclododecanone oxime in the sulphuric acid concentration range studied.

As the constants quoted below show, even in 90% acid cyclohexanone oxime is found almost completely as the protonated species $RNOH_2^+$. In 90% acid for cyclododecanone oxime the concentrations of the $RNOH_2^+$ ions and $RNOH_2^+.HSO_4^-$ species are commensurate. Therefore, for these oximes the product $k_{eff}a_{H_2O}$ does not stay constant. For suberone oxime and cyclopentanone oxime, the salt formation constant K_c' can be determined from the kinetic data for solutions of the acid where the relative concentrations of the $RNOH_2^+.HSO_4^-$ species and $RNOH_2^+$ ions are commensurate. If

$$C_{RN^+HSO_4^-} \ll C_{RNOH_2^+.HSO_4^-} + C_{RNOH_2^+},$$

then

$$k_{eff} = \frac{k_{true}}{K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}} + K_2' a_{H_2O}}. \qquad (13)$$

Eqn. (13) can be transformed:

$$\frac{1}{k_{eff} \cdot a_{H_2O}} = \frac{K_2' K_c'}{k_{true}} \cdot \frac{h_0}{a_{H_2SO_4}} + \frac{K_2'}{k_{true}}.$$

This equation describes the variation of k_{eff} with h_0, $a_{H_2SO_4}$, and a_{H_2O} and allows K_c' and K_2'/k_{true} to be calculated. Fig. 5 shows the variation of $1/k_{eff}a_{H_2O}$ with $h_0/a_{H_2SO_4}$ for suberone oxime.

The salt formation constant K_c' at 25° is 0.29 ± 0.02 for suberone oxime and 0.1 ± 0.02 for cyclopentanone oxime.

The ratio $k_{true}/K_2'K_c'$ is calculated from the variation of k_{eff} on a_{H_2O}, h_0, and $a_{H_2SO_4}$ for acid solutions where

$$C_{RNOH_2^+} \gg C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-},$$

If the limiting rate constants observed in oleum are true rate constants, then in dilute oleum there should be a transitional region where both the reactive form $RN^+.HSO_4^-$ and the ions $RNOH_2^+$ are present in commensurate concentrations.

In that region the effective rate constant should be given by the equation:

$$k_{eff} = \frac{k_{true}}{1 + K_2' K_c' \frac{a_{H_2O} \cdot h_0}{a_{H_2SO_4}}}. \qquad (14)$$

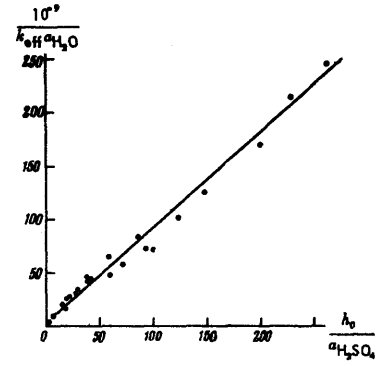


Fig. 5. Variation of $1/k_{eff}a_{H_2O}$ with $h_0/a_{H_2SO_4}$ for the Beckmann rearrangement of suberone oxime in sulphuric acid at 25°.

This equation can be used to calculate the value of k_{true} and $K_2'K_c'$. However, the true constants k_{true} calculated by Eqn. (14) are greater than the limiting values of the rate constants. For example, at 25° the limiting value of k_{eff} is 1.05 min^{-1} for cyclohexanone oxime, and the value of k_{true} calculated from Eqn. (14) is 1.35 ± 0.05 min^{-1}. For cyclopentanone oxime the limiting value of k_{eff} is 0.31 min^{-1} and the calculated value 0.6 ± 0.2 min^{-1}. Consequently, the limiting values of the rate constants in this instance do not correspond with the true values, that is, in solutions where k_{eff} no longer depends on the composition of the medium the reagents are not completely found in the reactive form. This is connected with the fact that in oleum containing 5–11% SO_3 the value of the constant $a_{H_2O}h_0/a_{H_2SO_4}$ (see Table 14) and therefore the degree of conversion of the oxime into the reactive form $RN^+.HSO_4^-$ does not change as the SO_3 concentration in the solution is varied.

Table 15 gives the values of the k_{true}, K_c', K_2', and $K_2'K_c'$ at 25° for four alicyclic ketoximes. K_2' and K_c' could not be calculated separately for cyclohexanone oxime. There are spectroscopic results which support the appearance of a new form of the oxime in the solutions of the acid where the

TABLE 14. Values of $\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}}$ for oleum at 25°.

SO_3, wt. %	5	6	7	8	9	10	11
$\log a_{H_2O}$	−11.40	−11.50	−11.58	−11.66	−11.73	−11.77	−11.82
H_0	−12.90	−12.98	−13.04	−13.1	−13.15	−13.21	−13.26
$\log a_{H_2SO_4}$	9.50	9.49	9.48	9.47	9.46	9.46	9.45
$\log \frac{a_{H_2O}h_0}{a_{H_2SO_4}}$	−8.0	−7.99	−8.02	−8.03	−8.04	−8.02	−8.01

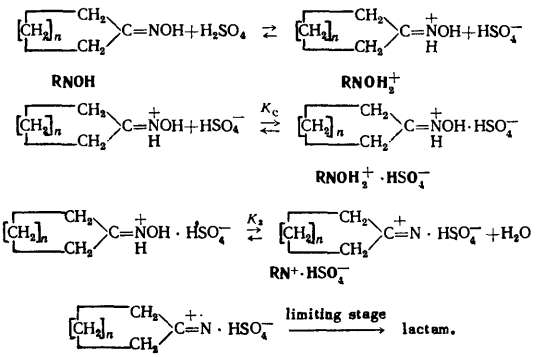
TABLE 15.

Oxime	k_{true}, min^{-1}	K_c'	$10^6K_2'$	$K_2'K_c'$	E_{true}, kcal $mole^{-1}$	log A_{true}	ΔH_{298}, kcal × × $mole^{-1}$
Cyclopentanone oxime	0.6±0.2	0.1±0.02	(2±1)·10^1	(2±1)·10^8	23.7±0.2	15.3±0.3	−7.0±2
Cyclohexanone oxime	1.35±0.05	—	—	(2.7±1)·10^7	21.5±0.2	13.6±0.17	—
Suberone oxime	0.96±0.04	0.29±0.02	(3.0±0.3)	(0.87±0.15)·10^8	23.5±0.2	15.4±0.2	−10±2
Cyclododecanone oxime	4.4±1.5	0.49±0.3	(5.7±1.9)	(1.9±0.9)·10^8	20.6±0.2	14.0±0.25	—

rate constant of the Beckmann rearrangement rises sharply. Fig. 6 shows the dependence of the molar absorptivity of cyclohexanone oxime at λ = 222 nm as a function of the concentration of sulphuric acid and oleum. As Fig. 6 shows, precisely in solutions where the H_2SO_4 concentration is over 99% and also in extremely dilute oleum the molar absorptivity of the oxime at λ = 222 nm rises sharply. This wavelength does not lie at the maximum absorption of the oxime; it is selected because the change in its absorption intensity was determined by the rate of the Beckmann rearrangement. Since this rise occurs in a rather narrow range of acid concentrations (from 99.9% H_2SO_4 to 0.1% SO_3) the possibility of explaining this by the displacement of the absorption maximum is excluded. Such effects are observed during the appearance of new forms of a substance which are distinguished from the other forms by the absorption coefficients at definite wavelengths.

In this way, on the basis of the results described, it follows that alicyclic ketoximes in concentrated sulphuric acid are present as four equilibrium forms: the un-ionised form, the protonated form, ion pairs, and dehydrated ion pairs. The form reactive in the Beckmann rearrangement is the dehydrated ion pair.

The mechanism can be represented as follows:



This mechanism does not differ in principle from that of Kuhara and Chapman proposed for the Beckmann rearrangement in non-aqueous solutions. According to Kuhara and Chapman the reactive form is the ester of the oxime and the acid. The results quoted do not agree with the mechanism proposed by Pearson and Ball[37]. According to them the ion pairs $RNOH_2^+.HSO_4^-$ should be reactive. As already mentioned above, the relative concentration of these falls in the sulphuric acid concentration region where there is a rise in k_{eff}. The limiting stage for the Beckmann rearrangement of alicyclic ketoximes can be either that of ion pair dissociation (rupture at the –N–O– bond) or that of rupture of the $-\overset{\diagdown}{C}-\overset{\diagup}{C}-$ bond of the ring in the $RN^+.HSO_4^-$ species. Since

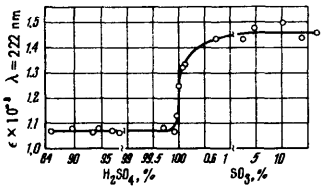
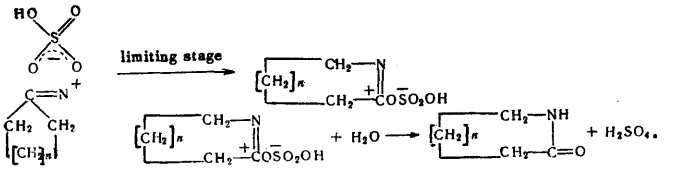


Fig. 6. Variation of the molar absorptivity (ϵ, litre mole^{-1} cm^{-1}) of cyclohexanone oxime at λ = 222 nm with the H_2SO_4 concentration.

the hydrated salt $RNOH_2^+.HSO_4^-$ is in equilibrium with the $RNOH_2^+$ cations, it can be suggested that the salt $RN^+.HSO_4^-$ is also in equilibrium with the products of its dissociation (RN^+ and HSO_4^-). In every instance ionisation, that is, rupture of the bond between nitrogen and oxygen, can proceed much more rapidly than rupture of a $-\overset{\diagdown}{C}-\overset{\diagup}{C}-$ bond and ring. It therefore seems likely that the limiting stage is the breaking of the $-\overset{\diagdown}{C}-\overset{\diagup}{C}-$ bond in the oxime. The breaking of a C–C bond and the formation of a C=N bond can proceed during the transfer of the positive charge from the nitrogen atom to the carbon atom. The HSO_4^- anion apparently assists the transfer of charge. In acids with a low water concentration and in oleum the dehydrated protonated form of the lactam is formed during the rearrangement. Hydration takes place during dilution of the reaction product with water.

Scheme of the limiting stage



In concentrated oleum, dehydrated ion pairs $RN^+.HS_2O_7^-$ can be formed:

$$2\,RNOH + 3\,H_2S_2O_7 \rightleftarrows 2\,RN^+ \cdot HS_2O_7^- + 2H_2SO_4.$$

As noted above, "Beckmann mixture" – consisting of a mixture of acetic acid and acetic anhydride, saturated with gaseous hydrogen chloride – is often used for preparations. Starting from the mechanism of the Beckmann rearrangement in sulphuric acid, the catalytic action of "Beckmann mixture" can be explained. For carrying out the process it is necessary to have an acid medium to bring about ionisation of the oxime. Since oximes are usually strong bases, the hydrochloric acid present in the "Beckmann mixture" is sufficient for this purpose. In the presence of an excess of acetic acid an ion pair (or salt of the oxime) can be formed. For the formation of the reactive form it is necessary that the salt consisting of the protonated form of the oxime and the anion of the acid be dehydrated. Judging from the available data the dehydration proceeds to an appreciable degree at very low activities of water. For example, in sulphuric acid the ion pairs of alicyclic ketoximes are dehydrated to a significant extent in the solutions where the water activity is less than 10^{-5}–10^{-6}. The presence of the anhydride in the mixture allows a low activity of water to be maintained in the solution. The water formed in the dehydration of the oxime in this medium is used up in the hydration of the anhydride and the activity of the water does not increase.

VI. TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES IN SULPHURIC ACID AND IN OLEUM

For the same concentration of sulphuric acid or oleum the rate constants of the Beckmann rearrangement k_{eff} at different temperatures fit the Arrhenius equation:

$$k_{eff} = Ae^{-E_{eff}/RT}.$$

TABLE 16. Activation energy E and preexponential factor A, s^{-1} of the Beckmann rearrangement of alicyclic ketoximes in sulphuric acid and in oleum.

H_2SO_4, wt. %	E, kcal mole^{-1}	log A
Cyclohexanone oxime		
82.29	25.0±1	11.8±0,7
86.03	24.0±1	11.4±0,7
89.94	23.7±1	11.5±0,7
92.73	23.4±0.5	11.5±0,4
94.71	22.9±0.5	11.4±0,4
98.21	22.2±0.5	11.5±0,4
99.74	21.5±0.2	11.6±0,2
SO_3, wt. %		
2.22	21.5±0,2	14,0±0,2
7.1	21.5±0,2	14,0±0,2
15.4	21.5±0,2	14,1±0,2
30—80*	24.8±0,4*	
Cyclopentanone oxime		
H_2SO_4, wt. %		
91.74	25,9±1	12,2±0.8
93.70	25,9±0,5	12,4±0,4
95.42	25,4±0,5	12,3±0,4
97.18	23,6±0,5	11,5±0,4
99.85	23,4±0,5	12,9±0,4
SO_3, wt. %		
5.5	23,7±0,2	15,1±0,15
27	23,7±0,2	15,1±0,15
Cyclododecanone oxime		
88,07	25,6±1	12,5±0,7
90,33	24,7±1	12,0±0,4
93,29	24,7±0,5	12,3±0,4
95,67	23,8±0,5	12,0±0,4
97,67	22,9±0,5	11,7±0,4
SO_3, wt. %		
1,38	21,1±0,2	13,7±0,15
3,86	20,6±0,2	13,5±0,15
11,4	20,6±0,2	13,5±0,15
33	20,6±0,2	13,5±0,15
Suberone oxime		
H_2SO_4, wt. %		
85,34	29,8±1	14,6±0,7
87,89	29,3±1	14,5±0,7
90,30	28,0±1	13,9±0,7
93,20	26,6±0,5	13,3±0,4
95,23	26,1±0,5	13,1±0,4
97,13	25,7±0,5	13,9±0,4
98,05	26,1±0,5	13,6±0,4
99,46	26,1±0,5	14,1±0,4
99,65	26,1±0,5	14,4±0,4
SO_3, wt. %		
7,5	23,5±0,2	15,10±0,15

* These quantities were obtained in work where the oxime concentration was ~ 0.5 M and in addition to the oxime a lactam was added (14 g lactam per 15 g oleum).

The activation energy which can be found from the Arrhenius equation depends on the concentration of sulphuric acid in solution. Table 16 gives the values of log A and E_{eff} for the rearrangement of cyclopentanone oxime, cyclohexanone oxime, suberone oxime, and cyclododecanone oxime in solutions of sulphuric acid and in oleum from published data [23-26]. As the acid concentration is raised the activation energy falls. For example, with suberone oxime, E_{eff} = 29.3 kcal mole^{-1} in 87–89% acid and 23.5 kcal mole^{-1} in oleum with 7.5 wt. % SO_3. In solutions where almost all the oxime is in the reactive form the observed activation energy is constant. For example, in the rearrangement of cyclohexanone oxime the activation energy is constant in the range from 99.74% H_2SO_4 to 15.4% SO_3. To explain what the activation energy calculated by the Arrhenius equation represents it is necessary to analyse Eqn. (12) which expresses the dependence of k_{eff} on the quantities a_{H_2O}, $a_{H_2SO_4}$, and h_0. On taking into account the temperature dependence of the constant this equation must be written as:

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\cdot e^{\frac{-E_{true}}{RT}}}{1+\dfrac{B_2 e^{\frac{\Delta H_2}{RT}}\cdot B_c e^{\frac{\Delta H_c}{RT}}\cdot B_{H_2O} e^{\frac{-\Delta H_{H_2O}}{RT}}\cdot B_{h_0} e^{\frac{-\Delta H_{h_0}}{RT}}}{B_{H_2SO_4}\cdot e^{\frac{-\Delta H_{H_2SO_4}}{RT}}} + B_2\cdot B_{H_2O} e^{\frac{\Delta H_2-\Delta H_{H_2O}}{RT}}},$$

where E_{true} and A_{true} are the true activation energy and true preexponential factor, ΔH_2 and ΔH_c the standard changes in enthalpy of the dehydration and dissociation of the ion pair $RNOH_2^+.HSO_4^-$, and B_2 and B_c the entropy multipliers of the equilibrium constants K_2' and K_c'. ΔH_{H_2O}, ΔH_{h_0}, and $\Delta H_{H_2SO_4}$, and B_{H_2O}, B_{h_0}, and $B_{H_2SO_4}$ are the heats and entropy factors which characterise the change in the activity of water, the acidity, and the activity of sulphuric acid with temperature.

In solutions where

$$C_{RN^+.HSO_4^-} \gg C_{RNOH_2^+} + C_{RNOH_2^+.HSO_4^-},$$

$$A_{eff}\,e^{-E_{eff}/RT} = A_{true}\,e^{-E_{true}/RT},$$

and the activation energy and preexponential factor given by the Arrhenius equation will be the true values. In oleum, where the rate constant of the rearrangement does not change, ~ 70% of the total concentration of the alicyclic ketoximes studied are in the $RN^+.HSO_4^-$ form. Therefore, the activation energy and preexponential factor determinable under these circumstances are the true ones.

In relatively dilute solutions of acid§ almost all the oxime is present in the form of the ion pairs $RNOH_2^+.HSO_4^-$:

$$C_{RNOH_2^+.HSO_4^-} \gg C_{RNOH_2^+} + C_{RN+HSO_4^-}.$$

Here:

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\,e^{\frac{-E_{true}}{RT}}}{B_2 e^{\frac{\Delta H_2}{RT}}\,e^{\frac{-\Delta H_{H_2O}}{RT}}},$$

and

$$-E_{eff} = -E_{true} - \Delta H_2 + \Delta H_{H_2O}.$$

Such conditions are observed, for example, for suberone oxime in the range 85.3–90.3% H_2SO_4 and for cyclopentanone oxime in the range 91.74–96.2% H_2SO_4. It now becomes possible to determine ΔH_2 for the oximes mentioned. The values of E_{eff} and ΔH_{H_2O} for 90% sulphuric acid can be used for the calculations. Table 16 gives the values of E_{eff}; ΔH_{H_2O} = 5.0 kcal mole^{-1}. This quantity is calculated from the temperature dependence of the pressure of water vapour over solutions of the acid, which are taken from a handbook [43]. ΔH_2 is -7.0 ± 2 kcal mole^{-1} and -10 ± 2 kcal mole^{-1} for cyclopentanone oxime and suberone oxime respectively. In acid solutions where

$$C_{RNOH_2^+} \gg C_{RNOH_2^+.HSO_4^-} + C_{RN^+.HSO_4^-}$$

$$A_{eff}\,e^{\frac{-E_{eff}}{RT}} = \frac{A_{true}\,e^{\frac{-E_{true}}{RT}}\cdot B_{H_2SO_4}\,e^{\frac{-\Delta H_{H_2SO_4}}{RT}}}{B_2 e^{\frac{\Delta H_2}{RT}}\cdot B_c e^{\frac{\Delta H_c}{RT}}\cdot B_{H_2O} e^{\frac{-\Delta H_{H_2O}}{RT}}\cdot B_{h_0} e^{\frac{-\Delta H_{h_0}}{RT}}}$$

and

$$-E_{eff} = -E_{true} - \Delta H_2 - \Delta H_c + \Delta H_{H_2O} + \Delta H_{h_0} - \Delta H_{H_2SO_4}.$$

This condition is observed for solutions of the acid in the range 99.4–100% H_2SO_4. In connection with the fact that for such solutions the enthalpies ΔH_{H_2O}, ΔH_{h_0}, and $\Delta H_{H_2SO_4}$ are still unknown it seems impossible to calculate the value of ΔH_c. It should be noted that in the intermediate region where the $RNOH_2^+.HSO_4^-$ and $RNOH_2^+$ concentrations are commensurate, in the general example the rate constants at different temperatures should not obey the Arrhenius equation, since the expression for k_{eff} includes the sum of two quantities with exponential factors. However, for a narrow temperature interval the Arrhenius equation is satisfied. The effective activation energy cannot then be presented in the form of a sum of E_{true} and the change in the

§ Here by relatively dilute solutions of sulphuric acid we mean solutions in which the H_2SO_4 concentration is < 90 wt.%.

enthalpies of the equilibrium processes. This is also true where the concentrations of $RNOH_2^+$ and $RH^+.HSO_4^-$ are commensurate.

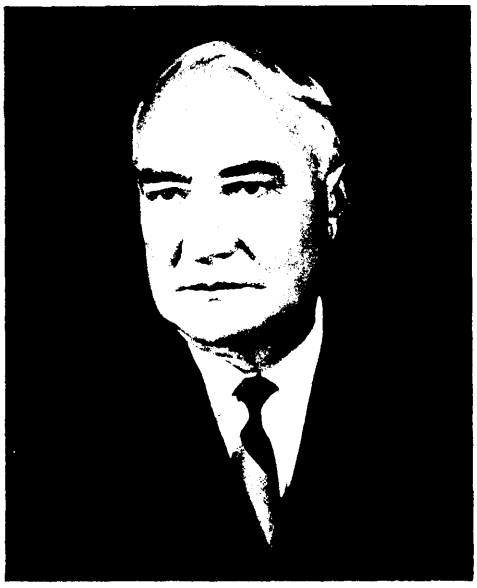
Table 15 gives the equilibrium constants K_2' and K_c', the product $K_2'K_c'$, E_{true}, and A_{true} for the four alicyclic ketoximes, and shows that E_{true} is less for ketoximes with an even number of carbon atoms than for those with an odd number of carbon atoms. This regularity is observed also for the activation energy of the Beckmann rearrangement of the oxime *p*-toluenesulphonates in chloroform[27]. From Heldt's results[27], the activation energies are 27 ± 1.3 and 23.4 ± 1.1 kcal mole^{-1} for cyclopentanone and cyclohexanone oximes and 24.4 ± 1.1 and 21.8 ± 1.2 kcal mole^{-1} for cycloheptanone and cyclo-octanone oximes respectively. For cyclohexanone oxime the preexponential factor is 4×10^{13} s^{-1}. This quantity is close to the normal preexponential factors for unimolecular reactions. For the remaining three oximes the intrinsic preexponential factors are greater than the normal values.

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RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

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VALENTIN ALEKSEEVICH KARGIN

Dear Valentin Alekseevich!

The Editorial Board of the journal "Uspekhi Khimii" convey to You their heartfelt greetings on the occasion of your sixtieth birthday and the completion of 45 years of your working life.

As an eminent physical chemist in our country, You have made a great contribution to the development of colloidal chemistry, polymer science, and also Soviet polymer industry. The wide range and depth of the problems of polymer science which You have solved, thereby gaining fundamental new knowledge in this field, have earned You the profound respect of scientists and industrial workers, both in our country and beyond its boundaries.

The Editorial Board of the journal "Uspekhi Khimii" wish You, dear Valentin Alekseevich, good health and new creative successes in your chosen branch of chemical science.

The Editorial Board of the Journal "Uspekhi Khimii"

U.D.C. 541.6:678.43/44

THE SUPERMOLECULAR STRUCTURE OF RUBBERS

V. A. Kargin, Z. Ya. Berestneva, and V. G. Kalashnikova

For a long time polymers were regarded as systems consisting of disordered, entangled, folded molecular chains. Crystallisation was thought to be the only possible ordered process in such systems.

However, a number of studies carried out in recent years failed to confirm these ideas on the structure of polymers. It was shown that, when polymers crystallised, spherulites with well defined boundaries and single crystals, much longer than the molecular chains, were formed. Geometrical considerations alone indicated that such structures could not be formed in a system of entangled molecular chains, and the hypothesis was therefore advanced that even amorphous polymers contain ordered elements [1,2].

The electron microscope studies of Kargin and coworkers showed that polymers with rigid molecular chains in the amorphous state are in fact well ordered systems [3-10]. Supermolecular structures may arise in these systems without a phase transition, the primary elements of these structures being globules or packets of molecular chains.

This ordered arrangement appears to be of a fluctuation type. Quite recently it was found that large structures, with dimensions up to several hundred microns, may arise in rigid-chain polymers [11-13]. Moreover, a number of experimental results indicate the presence of ordered arrangements of molecular chains in polymers melts [14,15]; there is also evidence that packet formations occur in dilute solutions of polymers [16,17].

Examination of the structure of solid polymers would be expected to show that the most disordered arrangement of molecular chains occurs in polymers with flexible molecular chains, known as elastomers, which are most similar in their physical state to liquids. The first X-ray structure studies did in fact show that the structure of rubbers is very similar to the structure of poorly ordered liquids [17]. The establishment of the kinetic theory of high elasticity promoted the development of the idea that elastomers consist of systems of entangled molecular chains [18-28]. However, the correctness of the assumptions made in setting up a model for the structure of rubbers within the framework of the theory of high elasticity has long been the subject of doubt. Thus Treloar noted that it is necessary to take into account intermolecular forces which hold the rubber molecules together at definite points, or even regions, with the formation of a three-dimensional network [29].

Bunn put forward the hypothesis that in rubbers the molecular chains are not arranged in an entirely random manner, but that regions of relative order occur in which the molecules are roughly parallel [30]. The same molecule passes through an ordered region and a completely disordered region.

Moreover, it has been suggested in a number of experimental papers that ordered formations occur in rubbers. Thus, examination of the mechanical properties of thin films of natural rubber showed that these films may contain some kind of structural units with dimensions of about 200 Å. [31]

A study of the dependence of the coefficient of diffusion of macromolecules of synthetic polyisoprene into amorphous natural rubber on the molecular weight of the latter also gave results suggesting that the molecular chains in natural rubber are ordered [32].

Recently it was found that the mechanical properties of films of natural rubber obtained from solutions depend on the initial concentration of the solution, provided that the concentration of the solution is not greater than 1%. [33] At concentrations higher than 1%, association complexes are formed in the solution, and the films obtained from such solutions have a more ordered structure, which is also reflected in their mechanical properties. The formation of some kind of ordered structures has been observed by the dilatometric method in butadiene-styrene rubber obtained by low-temperature polymerisation [24].

Since only structures with short-range order can occur within the limits of the amorphous state, it would be difficult to obtain any kind of results by studying the structure of amorphous rubbers by direct structural methods (for example, X-ray methods).

Investigation of the structure of rubbers by optical methods, and particularly by the methods of electron optics, showed the existence of ordered structures in rubbers. Thus, a study of mixtures of rubberlike polymers by phase-contrast microscopy showed that such systems were heterogeneous [34]. It was shown that in these systems mixing of the rubbers down to molecular dimensions does not occur; the mixture always consists of alternating characteristic structures of varying density with dimensions of the order of one micron.

Finally, in recent years the highly sensitive electron microscope method has been used to study the structure of amorphous rubbers. However, several papers have failed to give definite results of any kind with regard to the processes by which structures are formed in rubbers. Because of the difficulty of preparing rubbers, the workers concerned obtained either completely structureless films [35-37], or a pattern of strands, sometimes forming a characteristic network of threads with spherical or elliptical thickenings of different sizes [37-40]. It is not possible to draw any conclusions as to the structure of rubbers from the torn film rubber patterns obtained in the work reported in these papers.

Later, Shon showed that small spherical particles, 30-55 Å in diameter, could be observed on the surface of films of a number of amorphous rubbers (copolymer of butadiene with acrylonitrile, Buna-K, natural rubber) [41]. The test preparation was obtained by the replica method with preliminary shadowing with iridium. The author concluded that the view that rubber is a system with entangled molecular chains with no microstructure is incorrect, but that, in fact, amorphous rubber consists of more or less spherical particles formed from individual folded molecules. The author developed this point of view in a subsequent paper [42]. It should be noted that the observed size of the particles is at the limit of the resolving power of the replica method used [43]. Consequently, these results cannot be considered reliable. Moreover, it was shown that the occurrence of good rubberlike elastic properties evidently cannot be related to the presence of globular structures [44]. Thus, the graft copolymer of methyl methacrylate and natural rubber has rubberlike elastic properties only when it is isolated from solution under such conditions that the natural rubber chains remain stretched, but the methyl methacrylate chains are twisted. If this is not so (natural rubber chains folded into globules and methyl methacrylate chains stretched), a hard, completely inelastic product is obtained. In the study of organic compounds in the electron microscope it is difficult to obtain images with sufficient contrast, since the scattering power of carbon atoms is low, and the slight differences in density at separate sections of the film do not give the necessary difference in electron densities to provide contrast.

The structure of such polymers can only be evaluated when surface relief is present to provide the differences in thickness that are necessary for contrast. In the examination of crystalline polymers there is a considerable difference between different sections as a result of previous processes associated with the formation of structures, and because the polymer is solid.

Being elastomers, rubbers resemble liquids in their physical state. As they have a low modulus of elasticity, under the action of surface tension forces these systems tend to form spheres, or, in large amounts, they spread over the base, which leads to a smoothing of the relief that reflects the structure of the compounds.

To eliminate these difficulties, special methods of preparing the samples must be used [45]. Different solvents, or mixtures of solvents, can be used to reduce the solubility of rubbers. In this case, as the solvent is evaporated the concentration of the solution increases and, when the critical

concentration is reached, rubber separates from the solution. A poor solvent gives the best conditions for aggregation and the production of ordered structural formations. It is also possible, by the method of stretching films until rupture, to separate isolated structural elements from those that form the film.

The best results were obtained by preparing rubber samples from very dilute solutions at low temperatures [45,46].

Low temperatures promote the ordering process and give better structures for the amorphous state. Rapid cooling of a drop of rubber solution to a temperature below the glass temperature fixes the structure of the rubber in solution. When the solvent is removed at the same temperature, the rubber remains on the film holder in the solid state.

By using dilute solutions, isolated structural elements that may arise in elastomers can be obtained. Light petroleum has been used as a solvent; this gives a low glass temperature. It was shown by this method that amorphous rubbers are not structureless systems, but show a definite degree of order, characterised by the appearance of fibrillar structures about 200 Å in diameter and several microns long. Fig. 1 shows a picture of a sample of SKB rubber obtained under these conditions.

Similar structures were also observed in samples of type SKS-30 butadiene–styrene rubber [45,46]. Since SKS-30 and SKB rubbers have an irregular structure and cannot be crystallised, it is obvious that the structures observed in them are amorphous.

The formation of structures in elastomers at ordinary temperatures has been studied in the following way. The rubber was dissolved in a specially selected solvent and deposited on a film-base as a drop of solution, and the solvent was removed by different methods [45], or preparations were made as films on a water surface. The samples were shadowed with palladium to increase contrast.

The non-crystalline rubbers, SKS-30, SKB, and SKS-85, and also rubbers with a regular structure, such as natural rubber and chloroprene rubber of the "nairit A" type, give a pattern of striated structures in the amorphous state [45,47]. Thus Fig. 2 shows striations, up to about 1000 Å wide, arranged without order over the whole field of vision.

The first impression obtained from this pattern is that the film is made up of folds. For this reason, many workers who obtained similar patterns did not associate them with



Fig. 1. Na-butadiene rubber obtained from a dilute solution in petroleum ether at -75°.

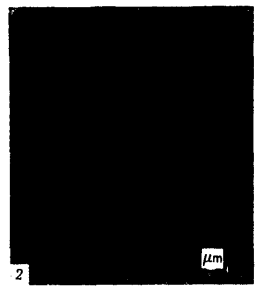


Fig. 2. Film of type SKS-30 rubber.

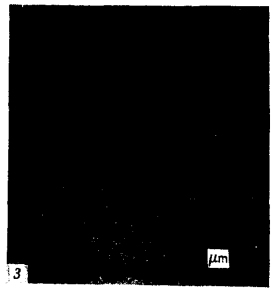


Fig. 3. Film of natural rubber obtained from a dilute solution in chloroform.

the process of structure formation. However, natural rubber gave the clearest striated structure pattern when the polar solvent chloroform was used (Fig. 3) [45,47]. In this case isolated structural elements forming a striated structure in the film can be observed. The presence of isolated structural elements during the preparation of samples at low temperature, and also at ordinary temperatures when a poor solvent is used, indicates that the striated structures observed result from processes leading to the formation of structures in amorphous elastomers.

The microstructure of the amorphous chain has no effect on the nature of the order in rubbers within the limits of the amorphous state. It has been shown that a reduction in molecular weight facilitates the process of structure formation. At low molecular weights the striated structure pattern is much more marked [45].

Up to now the finer features of this type of structure have not been elucidated. The possibility of ordered structures arising in amorphous polymers, and also the possibility of observing an intermediate state when a new phase separates from a homogeneous polymer solution may be imagined in the following way.

Every phase transition occurs abruptly within a very narrow temperature or concentration range. We cannot observe the transition itself because the time in which it occurs is too short compared with the times required for its observation. However, it is well known that, for example, in phase transitions in liquids, when one liquid separates into two phases, the change itself is preceded by the formation of clusters which are sometimes so large that the liquid becomes cloudy near the critical point although it still forms a single phase. The lifetime of these

clusters is also too short for direct observation. But there is no doubt that, given sufficient magnification, if we were able to observe such a liquid over very short periods of time, shorter than the relaxation period of the liquid, we would see the whole picture of the generation of order in the liquid: this would include the formation of clusters, their increase in size, and finally the formation of a dividing boundary and the production of a new phase. This would be the picture that Maxwell's imaginary "demon" would see if he could make observations over sufficiently short time intervals.

We cannot make such observations (which would show us the whole morphology of phase transitions), because ordinary molecules are too small, and their rate of movement is too great for the methods available to us. If we increase the size of the molecules by several orders of magnitude and obtain a corresponding reduction in their rate of movement by using polymeric compounds, we can observe the molecules and their aggregates directly with the electron microscope. The long relaxation time makes it possible to fix virtually any intermediate non-equilibrium state of the system observed, including all stages of a phase transition. By means of polymeric compounds, it is possible to set up a kind of enlarged model of a liquid the motion of whose molecules is greatly retarded, and to observe this model by means of the electron microscope.

Vulcanised chloroprene rubber which has been subsequently rolled until it is again in the soluble state has been studied. Values for the solubility of this rubber can then be easily chosen so that it is soluble in volatile solvents to the limited extent necessary for making preparations.

A 0.1–1% solution of rubber in CCl_4 was deposited on a pyroxylin base. As the drop of solution evaporated, the rubber concentration increased and, when the critical value was reached, two layers were formed, since the rubber preparations under examination were soluble to only a limited extent in this solvent. By regulating the rate of evaporation of the solvent it was possible to fix the different stages of formation of the new phase in the rubber solution.

Figs. 4*a*–4*c* and Fig. 5 show two series of such experiments. The first photograph (Fig. 4*a*) shows pictures of the still homogeneous rubber with typical striated structures. Then clusters arise with no sharp interfaces (Fig. 4*b*). Finally, a boundary begins to form but it is not closed immediately (Fig. 4*c*). Only in the final stage do we see particles of another phase with well marked boundaries typical of colloidal particles (Fig. 5).

Thus, intermediate stages in layer formation with the separation of a new phase can be observed in rubber. It is clear that intermediate and non-equilibrium states can exist for long periods even in elastic polymers, which have the most pronounced molecular mobility of all polymeric compounds, and that processes that are undetectable in low-molecular compounds can be observed when they occur in polymers.

After ordered structures had been found to occur in a number of rubbers, i.e. compounds that exist in a rubberlike state at temperatures roughly between -50°and +50°, it was suggested that the structures observed in rubbers are typical of all compounds that occur in the rubberlike state. In other words, the presence of striated structures is associated with rubberlike properties. It has recently been shown by several workers that isotactic polybutylene [48,49], chlorinated gutta-percha [50], and other compounds with rubberlike properties have a striated structure.

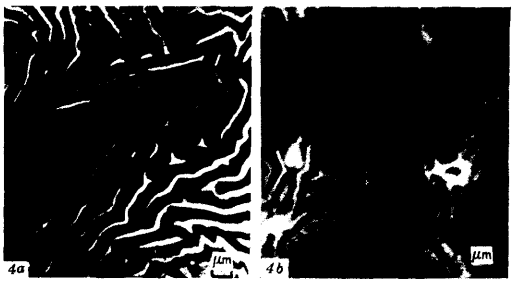




Fig. 4. Film of neoprene W rubber obtained from a solution in chloroform. The solvent was evaporated at room temperature. The film was kept in air for 3 to 5 days. Concentration of initial solution:
a) 0.1%; *b*) and *c*) 1.0%.

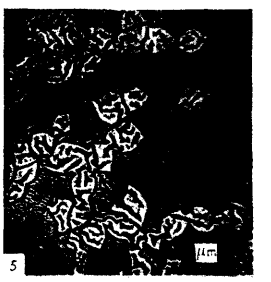


Fig. 5. Film of neoprene W obtained from a chloroform solution. The solvent was evaporated in a desiccator at room temperature over CCl_4. The film was kept for 3 to 6 days.

Thus, striated structures are typical of compounds that exist in the rubberlike state. In this connection it is of interest to examine the structure of fluorinated rubbers, which have a low degree of elasticity. It has been shown that the poor mechanical properties of cured rubber based on fluorinated rubbers are associated with special features in the supermolecular structure of these rubbers [51].

SKF-26 rubber is soluble in a very limited range of solvents — a number of ketones and esters. For this reason, acetone, ethyl methyl ketone, and isopentyl acetate have been used as solvents.

The structure of films is shown in Figs. 6*a* and 6*b*. Fig. 6*a* shows a film obtained from an acetone solution, and Fig. 6*b* a film from an isopentyl acetate solution.

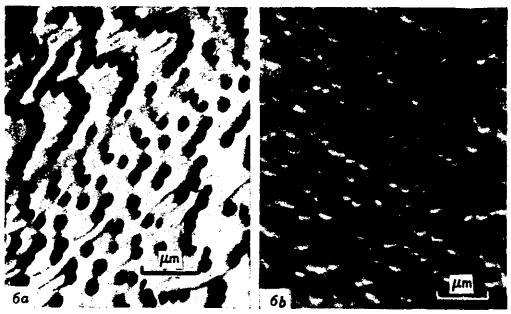


Fig. 6. Structure of films of type SKF-26 fluorinated rubber. The film was prepared:
a) from solution in acetone; *b*) from a solution in isopentyl acetate.

It is very clear that the films contain globular particles, irrespective of the nature of the solvent used; the diameter of the particles is about 1000 Å. A number of molecular chains contained in each globule may be calculated from the formula

$$n = \frac{\pi D^3 N \rho}{GM},$$

where n is the number of molecular chains, D the globule diameter, N the Avogadro number, ρ the density of the rubber, and M the molecular weight.

The mean molecular weight of the sample of rubber examined was 300 000. Calculations show that the globules are aggregates consisting of thousands of molecular chains. The value obtained is an upper limit; if the globule is deformed, this calculation gives high results. It has been found (Fig. 7) that block rubber, the structure of which was studied by the replica method, and also thin films, have globular structures, the size of the globules being the same in both cases.

It should also be noted that a characteristic feature of the structure of SKF-26 rubber is that only part of it is in the globular form; between the globules there is a kind of adhesive, the structure of which has not been elucidated (Fig. 6*a*).

The presence of two structural modifications is most clearly observed when samples are prepared from very dilute solutions (8×10^{-3} wt. % in ethyl methyl ketone).

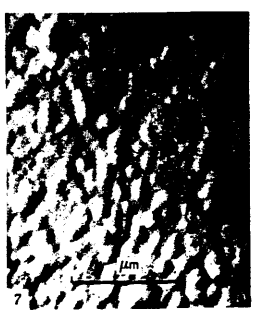


Fig. 7. Angular replica shadowed with palladium from SKF-26 block rubber.

Fig. 8*a* clearly shows an isolated globule and an aggregate of four densely packed globular particles in the neighbourhood of a portion of rubber the structure of which has not been elucidated. Sometimes fibrillar structures (Fig. 8*b*) may be observed in the structureless mass, which suggests that the adhesive may have a fibrillar structure.

The study of the properties of films stretched right up to the onset of rupture has confirmed this hypothesis. Fibrillar structures (Figs. 9*a*–9*c*) are clearly visible in stretched samples; it is clear that stretching reduces the number of globular structures, but the size of the globules does not change, and in the early stages of stretching they are only slightly deformed (Fig. 9*b*).

Sometimes, but not frequently, gradual unrolling of the globules may be observed, as shown in Fig. 9*c*. Obviously, during stretching there is both an abrupt and a gradual unrolling of the globules with the formation of fibrillar structures.

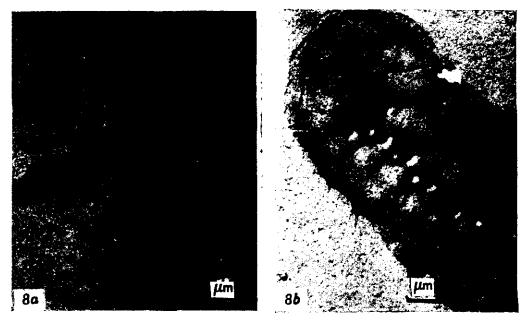


Fig. 8. (*a*) and (*b*) Type SKF-26 fluorinated rubber prepared from a dilute solution in ethyl methyl ketone.

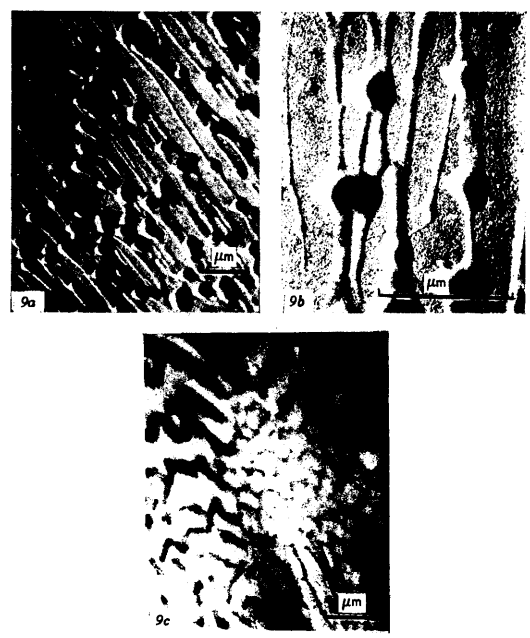


Fig. 9. (*a*, *b*, and *c*) Stretched film of type SKF-26 fluorinated rubber.

The globular structures in SKF-26 fluorinated rubber have the same dimensions of about 1000 Å over a wide range of concentrations of the solutions from which the samples are prepared. It may therefore be assumed that the globular structures arose in these rubbers during polymerisation. The diameter of 1000 Å appears to be the limiting diameter for a stable spherical particle of the fluorinated rubber. When the diameter increases beyond this limit, the globules are rearranged to form linear structures, because, when there are a sufficiently large number of molecules in the globule, the linear arrangement of these molecules may lead to denser packing and may also be more favoured energetically.

Thus, two structural modifications (globular and fibrillar) in equilibrium have been observed in SKF-26 fluorinated rubber. When the rubber is stretched, the globules abruptly unfold and the proportion of the fibrillar form increases. The development of elastic properties is probably associated with the existence of fibrillar formations and the possibility of globules unfolding. The presence of two structural forms in the rubber, with the globular form predominating, is probably responsible for the poor elasticity of this material.

Thus, electron microscope studies have shown that amorphous rubbers are ordered systems containing fibrillar and striated structures, in which globular structures may also occur. The formation of globular structures in rubber of the SKF-26 type leads to a reduction of its elasticity.

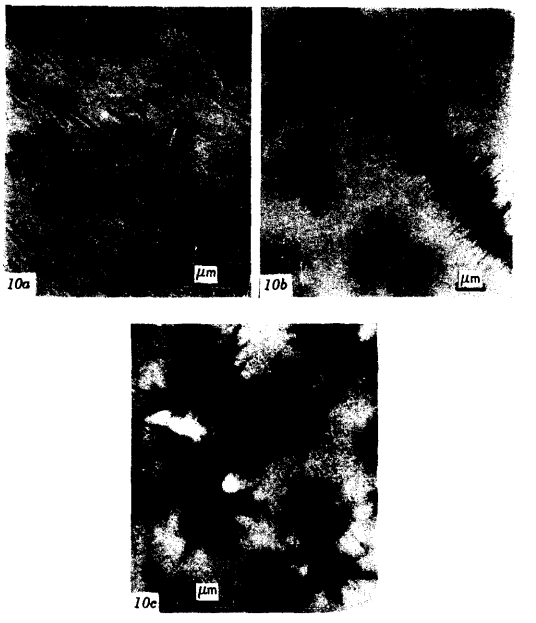


Fig. 10. Film of chloroprene rubber:
a) 1 day after removal of solvent; *b*) 2 days after removal of solvent; *c*) 7 days after removal of solvent.

It has been known for quite a long time that under certain conditions natural rubber, and also other elastomers with a regular structure, can be crystallised [17,27,52-72]. A great many papers have been devoted to the crystallisation of rubbers, and these have been exhaustively reviewed in a number of monographs [19,73,74].

The possibility that large crystalline structures of regular geometric shape may be formed in elastomers has cast doubt on the elastomer model proposed in the kinetic theory of rubberlike elasticity [75,76]. A somewhat modified model has been proposed for the structure of rubbers [76]; however, this does not differ fundamentally from the model of Kuhn, Mark, and Guth and is merely an unsuccessful attempt to set up a new theory for the structure of amorphous rubber which would explain the relative ease with which natural rubber tends to crystallise when the temperature is reduced. Campbell and Allen have made some interesting observations [24]: they used the polarisation microscope to study crystallisation in natural rubber and in polybutadiene obtained by low-temperature polymerisation. It was found that, when fused samples are repeatedly crystallised, the initial spherulite pattern is fully and precisely restored These results indicate that, when rubbers are fused, the molecular chains do not become entangled but a degree of order is maintained similar to that in the crystalline state.

Electron microscope studies of the structure of amorphous and crystalline rubber have shown that, at first, striated structures are observed, the finer structure of which is still not apparent. What part do these structures play in crystallisation? Is the process of crystallisation based on the striated structures present in the amorphous state, or are the crystalline formations the result of an independent ordering process? It has been shown experimentally that, in the initial stage of the crystallisation of polychloroprene (Fig. 10*a*), the striated structures are split into fine fibrillar formations, that is, "acicular" crystalline structures based on the striated structures in the amorphous state are formed in the process of crystallisation [45,46].

Thus, striated structures are the first to be formed, and then fibrillar structures of a different kind are formed. Crystalline fibrillar structures are formed from striated structures already present in the amorphous state. The final stage is the formation of spherulites (Fig. 10*c*).

The whole process of structure formation in elastomers has been observed in polychloroprene rubbers and isotactic polybutylene, which have rubberlike properties.

Figs. 10*a*–10*c* show the separate stages of the crystallisation of polychloroprene rubber. Thus, Fig. 10*a* shows the initial stage of the formation of fibrillar structures, which are later converted into acicular formations (Fig. 10*b*); finally, spherulite structures are formed (Fig. 10*c*).

Isotactic polybutylene shows a similar, but more marked structure formation (Figs. 11*a*–11*c*); here the crystallisation process leads to the formation of single crystals [48]. Fig. 11*a* shows the development of crystalline formations from striated structures. It is clear that the striated structures more or less split into separate fibrils. The further development of order leads to the coexistence of spherulites and crystalline surfaces (Fig. 11*b*), but crystallisation does not yet appear to have occurred throughout the bulk of the material. Further crystallisation leads to the growth and interpenetration of structures (Fig. 11*c*)

It has been shown that the presence of spherulites and lamellar crystalline formations in polymers with flexible chains does not inhibit the development of reversible deformations [49,76].

Thus, for many years the idea was widely accepted that rubbers are systems of entangled molecular chains; this idea arose from the kinetic theory of high elasticity. The correctness of this model was questioned almost as soon as

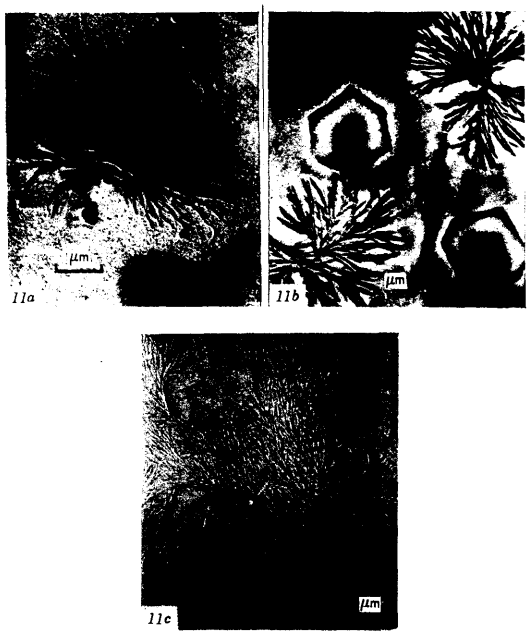


Fig. 11. *a*) Sample of isotactic polybutylene prepared from a dilute solution in toluene at 70° with rapid evaporation of the solvent and subsequent rapid cooling; *b*) and *c*) film of isotactic polybutylene obtained at 85° with subsequent slow cooling.

it had been proposed. In the 1940's experimental results began to appear that indicated indirectly the presence of an ordered arrangement of molecular chains in amorphous rubbers. The use of electron microscopy represented a new stage in the study of the structure of rubbers. By this method, it was shown that amorphous elastomers are not in fact systems of disordered entangled molecular chains, but systems containing well marked fibrillar and striated structures. Compounds in which this kind of structure was observed have good elastic properties.

Striated structures are the first stage in the development of order; these give rise to fibrillar structures, which in turn form more complex secondary molecular structures, spherulites, and crystals.

In the course of conversion into manufactured articles, rubbers are subjected to a number of treatments (plasticising, introduction of ingredients, vulcanisation). It is generally assumed that vulcanised rubber consists of a system of randomly arranged entangled molecular bundles. As with unvulcanised rubbers, the problem of structure formation in vulcanised rubbers is only considered from the point of view of the ability of the rubber to crystallise and of the effect of cross-linking on crystallisation. A certain volume around the cross-links is excluded from the total volume of material capable of crystallising; this is termed the volume "forbidden" to crystallise. The diameter of this volume around each cross-link is about 5100 Å.[77,88] It is assumed[79] that the existence of this volume only prevents the development of crystallisation in the direction along the axis of the molecules; crystallisation in a lateral direction is not limited, and the crystals formed are virtually indistinguishable from the crystals formed in the absence of cross-links. X-Ray structure analysis of crystallised vulcanised natural rubber has shown that the maximum rate of crystallisation of vulcanised rubbers is observed at the same temperature as the maximum for natural rubber[64,78-86], but the rate of crystallisation is inversely related to the thickness of the spatial network[86].

The principles that have been found to apply to vulcanised natural rubbers are also valid for the cured rubbers prepared from natural starting materials that were studied; these include 1,4-*cis*-polyisoprene, 1,4-*cis*-polybutadiene (SKD), and chloroprene rubbers[72,87]. The authors explained the phenomena observed on the basis of a model consisting of entangled molecular chains, with allowance for the effect of the "forbidden space" on crystallisation.

However, a number of experimental results are not in agreement with this model. Thus, melting points of crystals formed in the vulcanisation of natural rubber calculated on the basis of this model differ by one order of magnitude from the experimental results. Calculation shows that 1% cross-linking of chains should lower the equilibrium melting point of the crystallised network of natural rubber by 2–3 deg, whereas in fact the reduction is 20 deg.[80,88]

The hypothesis that crystalline formations have the same structure in vulcanised and unvulcanised rubber is also found to be only a first approximation; the results of X-ray structure analysis show that crystalline formations in vulcanised rubbers are much more defective[80].

On the basis of the X-ray structure analysis of vulcanisates of natural rubber, Lukin and Kasatochkin put forward the hypothesis that two kinds of intermolecular interaction occur in the amorphous vulcanisate[89]. The part of the compound with low molecular interaction is termed "gaseous", and the other part "liquid". The effects observed appear to indicate that the vulcanisate contains regions with different degrees of order. In this case, the greater molecular interaction corresponds to the more ordered regions.

In the vulcanisation of amorphous gutta-percha under different conditions, Kargin and Sogolova obtained products with different mechanical properties and probably with different degrees of order; this indicates that vulcanisates contain ordered formations[90,91].

The use of the electron microscope was a further step in the study of the structure of vulcanisates. Preparations were made by the replica method; these were taken from the tear surface of the vulcanisates or from a previously etched surface.

However, because of purely technical difficulties in the preparation of samples for electron microscope studies, identical results have not been reported. Thus, Lykin and Pechkovskaya observed in their electron microscope studies globular formations on the tear surface of vulcanisates of natural rubbers, but they considered it premature to draw any definite conclusions from this observation[92].

In other papers[93-95] dealing with the structure of vulcanisates of silicone rubbers, the authors conclude that the vulcanisates have globular structures, but the interpretation of the photographs is not unambiguous; they also show marked elongated structures of a fibrillar type.

Andrews and Braden obtained different results[96]. They made electron microscope studies of the structure of natural rubber vulcanisates after the surface had been etched with ozone; they found that the etched surface showed a system of fibrils, 500 Å in length and about 10 μm in diameter. Thus, etching showed that the samples had a heterogeneous structure. The authors explain the presence of this kind

of structure as the effect of strains set up in the samples during vulcanisation. From our point of view, these results indicate that ordered regions exist in the vulcanisates irrespective of the strains.

Electron microscope studies of the structural changes that occur during the vulcanisation of "nairit A" (by radiation, chemical, and thermal methods) gave the following results[45,97]. When chloroprene rubber is irradiated with γ-rays in a vacuum with the formation of a reticular structure, the original morphological pattern of the sample is not destroyed. Comparison of the infrared spectra of the samples irradiated in a vacuum with the spectra of the original samples shows that fairly extensive changes occur in the microstructure of the chain. The cross-linking of chains to form secondary molecular structures in the early stages of the irradiation probably prevents the destruction of these structures on further irradiation. Thus, when irradiated in a vacuum, the sample becomes cross-linked, considerable changes occur in the microstructure of the chain, and there is also probably considerable change to the amorphous state[98], but the type of arrangement of the molecular chains is unchanged.

When vulcanisation is carried out by the thermal method or by means of sulphur monochloride, the structure of the sample is gradually destroyed. Thermal vulcanisation was carried out at 153°, that is, at a much higher temperature than the melting point of rubber. Fig. 12*a* shows the initial structure of "nairit A"; crystalline molecular formations can be seen. Prolonged thermal vulcanisation destroys the structure (Fig. 12*b*). However, when low degrees of vulcanisation are applied, the morphological structures observed in the original rubber reappear with time; these range from amorphous band structures right up to more complete crystalline formations. Fig. 12*c* shows both striated and acicular formations.

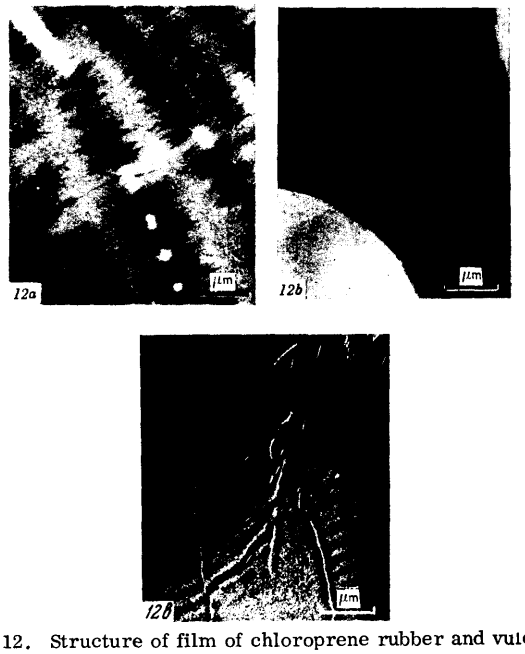


Fig. 12. Structure of film of chloroprene rubber and vulcanisate of type "nairit A" (thermal vulcanisation) in a vacuum: *a*) original rubber; *b*) after vulcanisation at 153° for 10 min; *c*) 9 days after vulcanisation.

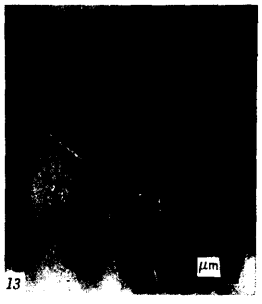


Fig. 13. Film of "nairit A" immediately after vulcanisation in air at 153° for 20 min.



Fig. 14. Film of "nairit A" 16 days after vulcanisation in air at 153° for 20 min.

Fairly large well formed surfaces with a regular geometrical shape (Fig. 13) can be observed immediately after thermal vulcanisation of samples for 20 min. Moreover, crystallisation continues with time and further spiral growth of crystals occurs on the surfaces first formed (Fig. 14). Thus, thermal vulcanisation may give rise to more nearly perfect structures than those in the original rubber.

Determination of the density of the network in portions of a sample has shown that, with vulcanisation for 20 min, cross-linking occurs at sections of the chain averaging 400 Å in length. With this kind of network, it is difficult to imagine how the polymer can crystallise, and in particular how higher structural forms, such as the crystals formed in this case, can arise, if it is assumed that the cross-links are statistically distributed between the individual polymer chains. It is probable that complete destruction of the secondary molecular structure in "nairit A" does not occur even at 153°, and, like any other chemical process, vulcanisation occurs at the boundaries separating these structures without destroying the structures themselves. It is only at high degrees of vulcanisation that bonds of this kind begin to be formed inside the structural elements.

In other words, vulcanisation is heterogeneous; otherwise the rubber would lose its ability to crystallise with the formation of higher structural forms.

In some cases it appears that not only does a vulcanisation network not prevent the formation of structures, but it may in fact promote this process. Thus, a study of carboxyl-containing polymers vulcanised with metal oxides has shown that the vulcanisates have an unusually high stability in unfilled mixtures[99]. However, the network formed is

easily destroyed by solvents; the energy required for destruction of the bonds is 1000–2000 cal mole^{-1}, that is, of the order of the energy of intermolecular interaction. This kind of network is therefore formed without chemical bonds. It has been suggested that basic salts are formed by the interaction between the polymer and the large oxide particles distributed in it; these sections also constitute the nodes of the network formed. The degree of order in these sections is probably much greater than in the remaining bulk of the polymer; this is due to the orienting action of the vulcanising agent. Here, too, large secondary molecular structures may be thinly distributed throughout the vulcanisate.

If the vulcanisation network arises at the boundary of structural formations, when the vulcanised rubber is destroyed elementary structural formations are retained; these are the component parts that make up more complex structures.

Processes of structure formation in disintegrated thermal vulcanisates of sodium-butadiene rubber (SKB) and neoprenes AS and W were studied in the following way. The vulcanisates were mechanically disintegrated to the soluble state in a laboratory rolling mill; they were then dissolved and deposited on a screen in the form of drops of solution. The disintegrated vulcanisates showed more ordered structures than the initial rubber (Figs. 15 and 16). Fig. 15*b* shows a more nearly perfect striated structure than the initial SKB rubber (Fig. 15*a*). Fig. 16*b* shows a spiral growth of crystals instead of the acicular structures of the original neoprene AS (Fig. 16*a*).

The processes of structure formation in disintegrated rubbers are retarded as the vulcanisation time is increased, that is, when the network becomes denser [100].

Thus, it has been shown that, when vulcanisates have been rolled and then brought into solution, secondary molecular structures are formed that differ in character from those of the original rubbers. This confirms that the cross-linking during vulcanisation is effected not between separate molecular chains, but between primary structural elements. On rolling, disintegration of vulcanisates appears to occur at cross-linking positions, the elementary structures being retained. The formation of secondary molecular structures in disintegrated rubbers can only be explained by the formation of a network between the primary structural elements; more complex secondary molecular structures are then formed from these elements, that is, vulcanisation is a heterogeneous process from the structural point of view.

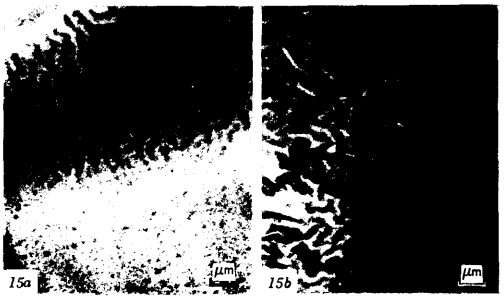


Fig. 15. *a*) Structure of original SKB rubber; *b*) SKB vulcanisate disintegrated to the soluble state by rolling.

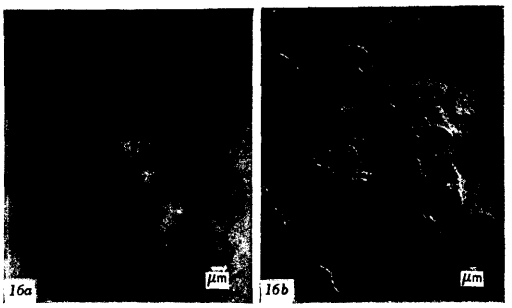


Fig. 16. *a*) Structure of original neoprene AS rubber; *b*) vulcanisate of neoprene AS disintegrated to the soluble state by rolling.

It has also been shown by the replica method that cured rubbers prepared from a number of different raw rubbers are ordered systems; they show structures similar to those observed in the raw rubbers [101]. The cured rubbers with the more ordered structures also have the best mechanical properties [102].

The introduction of low-molecular compounds (water, methanol, nonyl alcohol) increases structure formation in cured rubbers, and this is accompanied by an increase in strength [103].

All this is evidence for the lability of structure in vulcanisates and points to the importance of processes of structure formation in the treatment of rubbers.

Thus, for a long time rubbers were regarded as systems of entangled molecular chains. In the 1940's indirect experimental results began to appear indicating the presence of order in amorphous elastomers. This evidence was obtained both in the study of amorphous rubbers and in the study of special features of the crystallisation of rubbers with a regular structure. The use of electron microscope methods for studying the structure of rubbers and vulcanisates enabled the structure of amorphous rubbers to be elucidated, and the processes of structure formation in crystalline rubbers to be followed. It was shown that amorphous rubbers are ordered systems. Ordering processes occur in these, leading to the formation of striated structures 1000 Å in diameter, fibrillar structures 200 Å in diameter, and globular formations.

Rubberlike properties in elastomers are associated with the presence of striated, fibrillar structures. In studies on the structure of chloroprene rubber and isotactic polybutylene, the whole process of structure formation could be followed; striated structures are first formed in the amorphous state and then crystalline structures develop from these. The striated structures are an expression of pre-crystalline order in elastomers.

Vulcanisates, like rubbers, are ordered systems. Vulcanisation is a heterogeneous process that occurs at the boundaries of the structural elements present in the rubbers.

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POLYMERISATION OF CHEMICALLY ACTIVATED MONOMERS†

V.A. Kabanov

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In a recently published paper Kargin and Kabanov[1] discussed the problem of the polymerisation of complexed and organised monomers, which may be regarded as one of the new developments in the field of macromolecular synthesis. In the present review an attempt is made to develop and justify in greater detail some of the postulates put forward by Kargin and Kabanov.

1. INTRODUCTION

The conversion of a monomer M into a polymer P can be represented by the mechanism

$$M \rightarrow R^* \rightarrow P, \qquad (I)$$

where R^* are activated intermediates (growing chains). However, this mechanism does not reflect the interaction of M, R^*, and P with the medium, which often occurs in real systems. Therefore, extending mechanism (I), one should write

$$M(X)_i \rightarrow R^*(X)_j \rightarrow P(X)_k, \qquad (II)$$

where X represents the species of the medium interacting with the monomer molecules, with the active centres of the growing chains, and with the units of the polymer being formed (i, j, $k \geqslant 0$).

If the chemical interaction of the monomer with the medium results in an increase of the absolute rates of conversion or, when several modes of polymerisation are possible, in a relative increase of the rate of conversion by a particular pathway, chemical activation is said to obtain and the corresponding monomer is chemically activated.

Chemical activation of a monomer may be due to (1) the redistribution of electron density among the intramolecular bonds caused by the interaction between M and X, which we shall call the intramolecular effect or (2) a change in the nature of the intermolecular bonds between the reacting species accompanied by a change in their distribution and mutual orientation (for example, the formation in the system of organised aggregates favouring chain growth), which we shall call the intermolecular effect.

The presence in the systems of species X interacting with the monomer often affects more than just its reactivity. The addition of a monomer molecule combined with a species X to the initial active centre may result in the formation of a new active centre which is also capable of retaining the species X. Hence the possibility arises of a change in the reactivity (for example, activation) of the growing chains and even the possibility of polymerisation mechanisms which are not characteristic of the given monomer in relatively inert media.

Finally, the interaction between the species X, the initial monomer, and the units of the polymer being produced can appreciably alter the free energy of polymerisation. Indeed if the chemical potentials of the macromolecular units and monomer molecules in the presence of X are μ_{px}

† The contents of this article were presented at the International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, September, 1966.

and μ_{mx} respectively, the change in chemical potential on polymerisation is

$$\Delta\mu = u_{px} - \mu_{mx} = \mu_p - \mu_m + \overline{\Delta G}_x = \Delta\mu_0 + \overline{\Delta G}_x. \quad (1)$$

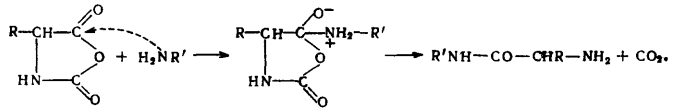
where μ_p, μ_m, and $\Delta\mu_0$ are the chemical potentials of the polymer and monomer and the change in chemical potential in an inert medium. $\overline{\Delta G}_x$ is the difference between the free energies of interaction of X with the polymer units and with the monomer.

Thus "chemical activation" opens up extensive possibilities of influencing the mechanism and thermodynamics of polymerisation reactions. The above considerations constitute the basis of the approach formulated and developed in recent years by Kargin and his school.

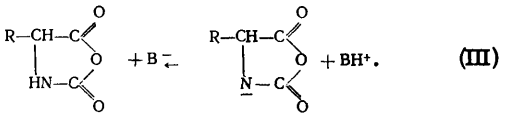
Certain examples, adduced to demonstrate a number of important aspects of the polymerisation of chemically activated monomers, are discussed below.

2. INTRAMOLECULAR EFFECT

A classical example is the polymerisation of *N*-carboxy-anhydrides (NCA) to polypeptides. The mechanism of this reaction has been examined in detail in Szwarc's review[2]. NCA are known to polymerise easily in the presence of bases (amines, alkalis, alkali metal alkoxides, and others). When primary amines are used as initiators, the initiation takes place as a result of the nucleophilic attack by the amino-group on the carbon atom of the carbonyl group of the monomer in position 5:

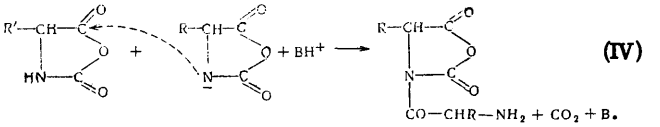


Chain growth takes place similarly, but with participation of the terminal amino-group of the chain being formed. However, this mechanism does not account for the experimental data when polymerisation is initiated by secondary amines or strong bases. Some years ago Bamford and Block[3] proposed another mechanism for the polymerisation of NCA, based on the hypothesis that in the presence of a sufficiently strong base the monomer exists in two forms described by the equilibrium:



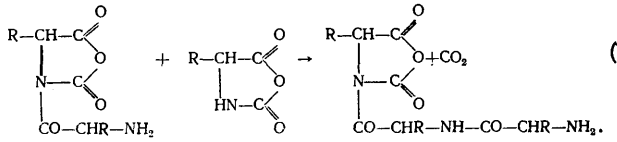
(III)

Initiation takes place as a result of the interaction between the "normal" and ionised monomer molecules:



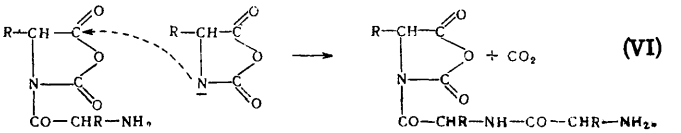
(IV)

This results in the formation of a bifunctional dimer, whose terminal amino-group can attack and add to the "usual" NCA molecule by the mechanism



(V)

At the same time the terminal cyclic group can be attacked by an ionised monomer molecule:

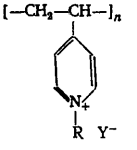


(VI)

Using ^{14}C-labelled initiators, Goodman and coworkers[4] and Scoffone and coworkers[4] confirmed this mechanism and showed that in the presence of tertiary amines and strong bases (in particular sodium methoxide) chain growth takes place mainly by mechanism (VI), i.e. by the addition of ionised NCA molecules, which react significantly faster than the initial molecules. Thus the interaction of NCA with strong bases results in its chemical activation (greatly enhanced nucleophilic character) by mechanism (III). Within the framework of the problem under discussion, the complex mechanism of the polymerisation of NCA must be assigned to one of the simplest limiting cases, since the activator (base) reacts only with monomer molecules and not with the growing chains [in mechanism (II) $i = 1$ and j, $k = 0$]. The alkali-catalysed polymerisation of caprolactam, studied in detail by Wichterle and coworkers[5], takes place similarly.

In the example just considered the activation is due to the chemical modification of the individual monomer molecules and not to the intermolecular bond between them, i.e. according to the classification adopted above the activation must be attributed to the intramolecular effect.

Systems in which the activator forms fairly strong bonds with monomer molecules, the active centres of the growing chains, and the units of the macromolecular molecules, i.e. constitutes a component of the polymer, can be assigned to the second limiting case. It has been shown recently[6-10] that in the interaction of 4-vinylpyridine (4-VP) with alkyl halides (Menshutkin reaction) in organic media (benzene, nitrobenzene, acetonitrile, dimethyl sulphoxide, propylene carbonate, and methanol) at -5° and above, instead of monomeric quaternary salts, the products isolated are high-molecular amorphous substances with the general formula

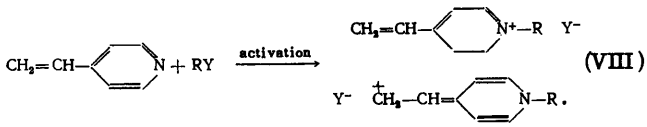


(VII)

which do not contain free pyridine base groups, i.e. spontaneous polarisation takes place. In the presence of an excess of 4-VP the formation of the polymer ceases as soon as the alkyl halide has been used up, and unreacted 4-VP remains in the system. This indicates a close relation between salt formation and polymerisation and that only 4-VP molecules which have undergone the Menshutkin reaction participate in the polymerisation. Strong inhibitors of radical polymerisation (benzoquinone, diphenylpicrylhydrazyl, and *N*-oxides) do not retard the reaction and do not affect the characteristic viscosity of polymers. This means that a radical mechanism of polymerisation can be excluded. When the reaction between 4-VP and ethyl bromide is carried out in acrylonitrile and in styrene, the resulting polymers do not contain nitrile and styrene units respectively, i.e. under the reaction conditions both styrene and acrylonitrile behave as solvents and do not copolymerise with 4-VP. This makes it possible to eliminate the

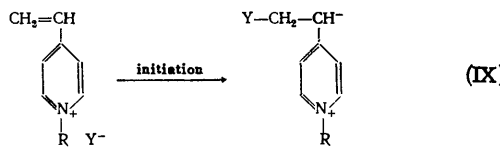
usual anionic and cationic mechanisms. The findings enumerated above necessitated the hypothesis that the polymerisation has a specific mechanism whereby only the molecules of the vinylpyridinium salts formed in the Menshutkin reaction are selectively polymerised. This mechanism was confirmed by detailed kinetic measurements (Aliev, Kabanov, Kargin)[8-10].

The first stage, which is rate-limiting for the process as a whole, is the Menshutkin reaction:



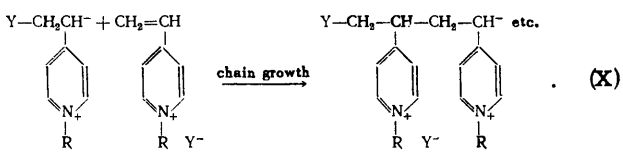
(VIII)

As a result of the appearance of a positive charge on the nitrogen atom in the monomeric salt, the π-electrons of the double bonds are appreciably displaced towards the pyridine ring, this being accompanied by a sharp increase in the electrophilicity of the double bond. The activated monomer now readily combines even with weak nucleophilic agents. The role of such an agent in the initiation reaction is fulfilled by the anion Y^-:



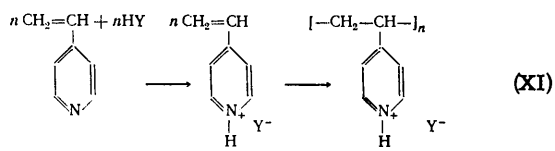
(IX)

[It should be noted that Eqn. (IX) bears a profound analogy to the well known pyridylethylation processes][11,12]. The zwitter-ion produced begins chain growth, by combining with the next molecule of the chemically activated monomer:



(X)

The molecules of 4-VP and other monomers cannot compete with those of the vinylpyridinium salt, in the first place because on addition of any other monomer to the active centre charges of opposite sign, which in the initial active centre interact via the π-bond system of the pyridine ring, would have to be separated, i.e. the energy of the system would increase significantly (loss of conjugation in the zwitter-ion and electrostatic effect). In the example examined the activator itself undergoes chemical reaction, forming a strong bond with the monomer and entering into the composition of the polymeric chain [in mechanism (II) i = 1 and j and k are equal to the degree of polymerisation], and cannot be removed from the polymer after the reaction. However, chemical activation of 4-VP (as well as that of 2-vinylpyridine) occurs also under the action of strong proton acids[6,10,13]. When 4-VP is mixed with sulphuric, nitric, toluenesulphonic, and other acids in benzene, ethyl ether, and other solvents at room temperature, the corresponding salts of poly-4-VP are formed:



(XI)

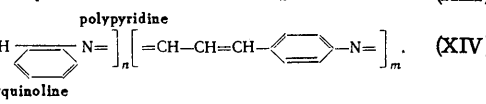
The mechanism of the polymerisation is probably largely similar to the one just described, but the subsequent treatment of the system with dilute alkali converts polyvinylpyridinium ions into polyvinylpyridine, i.e. the activator is readily removed from the polymer. It is striking that on addition of strong acids (in particular sulphuric acid) to 4-VP solutions in styrene the 4-VP salt produced immediately polymerises. Neither the excess 4-VP nor styrene are involved in the reaction. Thus the conversion of 4-VP into quaternary salts results in the generation of active centres with exceptional chemical selectivity. By virtue of the unusual nature of the active centres, the growing chains are capable of "selection" from the reaction system and can combine with N-alkylated or protonated monomer molecules.

The polymerisation and copolymerisation of complexed aromatic heterocycles (pyridine and quinoline) with ring opening may be regarded, in principle, as a closely related case[14-19]. The polymerisation of the stoichiometric complexes of pyridine and quinoline with zinc chloride has been investigated in detail between 250° and 370°:



(XII)

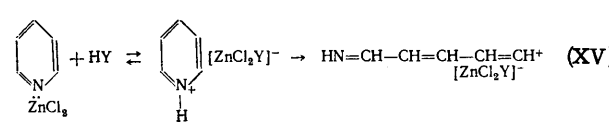
When melts of the pyridine complexes are heated above 330° and those of quinoline complexes above 250° in the presence of proton-donating initiators (HPO_3, H_2O, and pyridinium or quinolinium chlorides), high-molecular thermostable paramagnetic substances soluble in concentrated mineral acids are produced; their structure may be described by the formulae



(XIII)

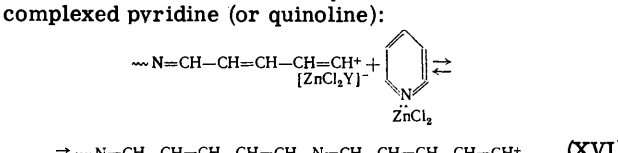
(XIV)

The kinetic role of the complex-forming agent probably consists in the polarisation of the nitrogen–carbon bond in the aromatic heterocycle which facilitates its heterolytic splitting when attacked by an electrophilic agent. Detailed kinetic studies[10,15-17] suggest that the following polymerisation mechanism is the most likely. Initiation in the presence of proton donors can be represented by the mechanism



(XV)

(for simplicity, only one of the pyridine molecules bound to each zinc chloride molecule is shown here). Chain growth occurs as a result of the attack by the carbonium cation on the complexed pyridine (or quinoline):



(XVI)

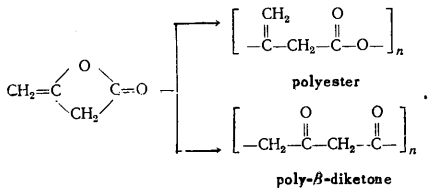
At the end of the reaction the polymer can be separated from the complex-forming agent by reprecipitation with water from concentrated mineral acids.

Chain growth in the polymerisation of aromatic heterocycles is reversible. For this reason, at a given temperature a limiting degree of conversion, determined by the equilibrium concentration of the monomer complex, is established in the system. The study of the temperature

variation of the limiting conversion showed that the polymerisation of pyridine and quinoline complexes is characterised by a lower limiting temperature (for the pyridine complex $T_{1.lim} \simeq 300°$, $\Delta H \simeq 13$ kcal mole^{-1}, and $\Delta S \simeq 19$ e.u., and for the quinoline complex $T_{1.lim} \simeq 240°$, $\Delta H \simeq 12$ kcal mole^{-1}, and $\Delta S \simeq 19$ e.u.). As shown above, these thermodynamic quantities include respectively the differences between the enthalpies and entropies of formation of the complex of the activator with the polymer and with the monomer.

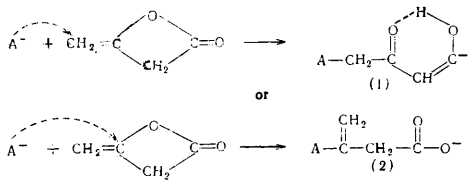
In the absence of complex-forming agents, polymerisation of pyridine and quinoline with ring opening cannot be achieved. Thus chemical activation of these monomers yields new polymers, which cannot be obtained by the usual methods of synthesis. Some years ago polymeric products were obtained by a similar procedure from nitriles by polymerisation at the C≡N bond[10,14,20-26]‡. The starting materials were complexes of nitriles with coordination-unsaturated metal halides.

Chemical reactions of monomers and growing chains with the species derived from the medium can influence the structure of the polymer units. Possibly this effect actually takes place in the polymerisation of diketen initiated by metallic magnesium[27]. It is known that, depending on the nature of the initiating agents and the reaction conditions, diketen can polymerise to a polyester[28] or a poly-β-diketone[29]:



(XVII)

The reaction of diketen with magnesium results in the formation of substances which initiate the anionic polymerisation of diketen (the initiation mechanism has been examined by Shul'gina et al.[27]). A copolymer is then formed, in which the ratio of polyester and poly-β-diketone units is approximately 1 : 1. The structure of each successive unit is determined by the mode of the nucleophilic attack on the vinyl group of the monomer by the growing anion:

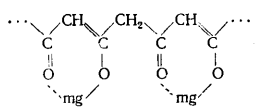


(XVIII)

or

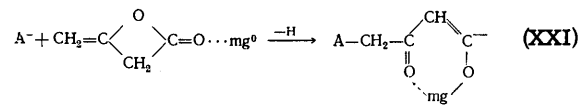
(XIX)

However, when the polymerisation is carried out in the presence of an excess of highly dispersed metallic magnesium (dispersed in the reaction system) hydrogen is evolved during the reaction and a polychelate, not containing ester units, is formed:



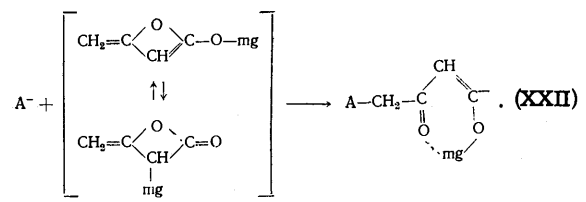
(XX)

After treatment with acid, the polychelate is converted into poly-β-diketone (mg represents one equivalent of magnesium). It may be supposed that in this case the polymerisation involves monomer molecules combined with magnesium and the reaction proceeds by one of the following mechanisms:



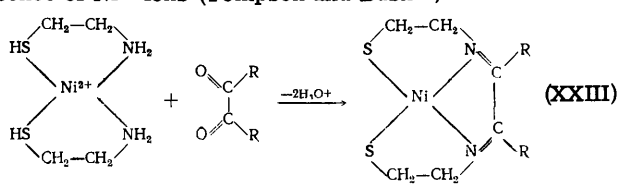
(XXI)

or



(XXII)

The chelate anion formed is more stable than anion (1) in mechanism (XVIII) and anion (2) in mechanism (XIX). For this reason, the reaction results exclusively in the formation of β-diketone units. In other words, the new monomer obtained in the reaction between diketen and magnesium is chemically activated for the formation of poly-β-diketone. It is noteworthy that in the chemistry of low-molecular compounds there are a number of cases where substances capable of coordinating the starting materials and the final products have a decisive influence on the mode of the chemical reaction (see, for example, Ref. 30). Of the numerous examples available, one may quote the synthesis of Schiff bases from β-mercaptoethylamine and α-diketones in the presence of Ni^{2+} ions (Tompson and Bush[31]):



(XXIII)

The reaction yields a compound with a significantly more stable chelate unit than the initial substance. In the absence of a complex-forming agent, thiazolines and mercaptals are formed instead of the Schiff base. The use of a similar principle in the synthesis of polymers may be of considerable interest.

3. INTERMOLECULAR EFFECT

In all the systems examined so far chemical activation must be regarded as due to an intramolecular effect. Although chemical interaction between the monomer and the species derived from the medium by no means always leads to a redistribution of electron density involving the reaction centres of the monomeric molecules responsible for polymerisation, such interaction can nevertheless lead to a considerable acceleration of polymerisation, i.e. to the activation of the monomer in the broad sense of the word, if it results in a change of the distribution of the reacting species, and (or) orientation of the reaction centres favouring chain growth (intermolecular effect).

An outstanding example is the initiation by benzoyl peroxide of the polymerisation of *p*-methacryloyloxybenzoic acid (MOBA) in the presence of *p*-cetyloxybenzoic acid

‡ The thermodynamic considerations concerning the polymerisation of complexed nitriles presented by Kargin et al.[20] are erroneous.

(COBA), investigated recently by Amerik et al.[32] In dimethylformamide solution MOBA polymerises in accordance with laws characteristic of the usual radical processes (reaction order with respect to the initiator 0.5 and with respect to the monomer 1.1). An equimolar mixture of MOBA and COBA forms smectic liquid crystals in the temperature range 87–133°. The structure of the smectic layer of such a crystal is shown in Fig. 1.

The rate of polymerisation and the molecular weight of the polymer formed in liquid crystals are significantly higher than in solution (at the same monomer concentrations the molecular weight changes from 5×10^4 to 6×10^5). The order of the reaction with respect to the monomer is close to zero. It is quite evident that the formation of hydrogen bonds between MOBA and COBA cannot influence directly the reactivity of the vinyl groups of the monomer. The acceleration of polymerisation and the increase of molecular weight are probably due to the existence in the system of labile monomeric "seeds", which, as shown earlier[33-35], favour the growth of polymeric chains. One cannot exclude the possibility that the "organised" disposition of double bonds in smectic layers can also influence the mechanism of the fundamental chain growth step. In view of this, the observed differences in the temperature variation of the microtacticity of polymers formed in solution and in liquid crystals are of considerable interest (Table 1).

In the polymerisation of MOBA in solution the percentage content of isotactic (i), heterotactic (h), and syndiotactic (s) triads in the polymer varies in the "normal" way [$\Delta(\Delta H^{+}) = 1025$ cal mole^{-1}; $\Delta(\Delta S^{+}) = 0.5$ e.u.]. In the liquid-crystal polymerisation the isomeric composition of the polymer differs significantly and is altogether independent of temperature [$\Delta(\Delta H^{+}) \simeq 0$; $\Delta(\Delta S^{+}) = 0.8$ e.u.]. The above data show at least a difference in the energy relations of the transition states in solution and in the liquid crystal. It

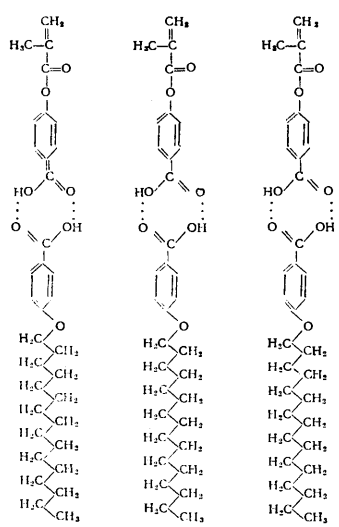


Fig. 1. The structure of the smectic layer of a liquid crystal complex of *p*-methacryloyloxybenzoic and *p*-cetyloxybenzoic acids[32].

TABLE 1. Temperature variation of the microtacticity of poly-*p*-methoxybenzoic acid (poly-MOBA)[32] measured by the NMR method after the conversion of poly-MOBA into poly(methyl methacrylate).

Polymerisation temperature, °C	In solution			In the liquid crystal		
	i	*h*	*s*	*i*	*h*	*s*
0	6.2	18.8	75.0			
40	7.0	23.3	69.7			
90	8.2	28.8	63.0	8.0	44.0	48.0
110	8.7	30.1	61.2	8.0	45.0	47.0
130				8.0	45.0	47.0

should also be noted that in the absence of COBA at temperatures above 100° the rate of depolymerisation of poly-MOBA is comparable with the rate of its formation. Therefore, when the reaction is carried out in solution, a polymerisation–depolymerisation equilibrium is established, and the yield of polymers does not reach 100%. Polymerisation in the liquid-crystal state at temperatures up to the melting point of the liquid crystals results in complete conversion of the monomer into the polymer. Thus in this case the activator not only influences the kinetics but also the thermodynamics of the polymerisation.

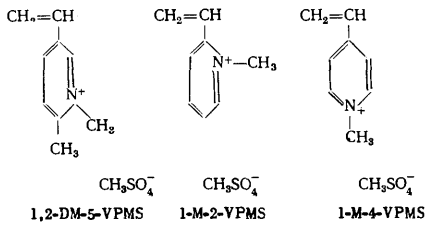
The intermolecular effect is shown "in a pure form" in polymerisation in canal compounds[36,37]. It is known that in the presence of certain organic substances urea and thiourea form tetragonal crystals with tubular channels of molecular diameter, which become filled with molecules of the organic substances. Certain vinyl compounds and dienes become arranged into linear sequences of molecules in such channels and can be rapidly polymerised under the action of accelerated electrons and γ- or X-radiation. When canal compounds of buta-1,3-diene with urea and dimethylbuta-2,3-diene with thiourea are irradiated with electrons, the corresponding crystalline *trans*-poly-1,4-dienes are formed[36,37], although the radiation-induced polymerisation of these monomers in the solid state or in solution always results in irregular polymers of mixed structure. The weak van der Waals interaction with the walls of the channels cannot lead to appreciable redistribution of electron density in the individual monomer molecule. Therefore the chemical effects shown in polymerisation in canal compounds, in particular the sharp increase in the relative rate of 1,4-*trans*-addition of dienes, must be attributed in the first place to the favourable mutual orientation of the double bonds of the initial monomeric sequences, i.e. to an intermolecular effect. Strictly speaking, even if the term "chemical activation" is applicable to the above phenomenon the same stipulations must be made as in the application of the term "chemical compound" to canal compounds.

Pursuing further this approach, one can cite the familiar phenomenon of the sharp increase in the rate of polymerisation in the crystallisation of liquid and vitreous monomers[33-35,38]. It has been shown that the acceleration is closely related to the formation at the interface between the crystalline and amorphous phases of mobile ordered aggregates of monomeric molecules — "labile seeds"[38] — i.e. is also due to an intermolecular effect. However, in this case the factors which lead to the formation of "labile seeds" are physical and not chemical in nature: the concept of "chemical activation" degenerates.

4. SIMULTANEOUS OCCURRENCE OF INTRA- AND INTER-MOLECULAR EFFECTS. MACROMOLECULAR "MATRICES"

In many cases the intramolecular and intermolecular effects occur simultaneously in chemical activation. It was noted above that the quaternary salts of 4-VP and alkyl halides polymerise spontaneously in organic media in statu nascendi. In accordance with the polarisation mechanism examined above, it is to be expected that quaternary salts of vinylpyridines with the double bond in position 5 or 3 and hence polarised to a lesser extent should show a smaller tendency towards spontaneous polymerisation. Indeed in the reaction between 2-methyl-5-vinylpyridine (MVP) and ethyl bromide, methyl iodide, dimethyl sulphate, and others in organic solvents (acetone, ethyl acetate, etc.) polymerisation does not occur: crystalline monomeric salts are precipitated. The salts of 4-VP and 2-VP whose anions exhibit relatively weak nucleophilic properties can also be obtained in a monomeric form in organic solvents at low temperatures. However, all these monomers polymerise spontaneously in concentrated aqueous solutions.

Kargin et al.[7,8,10,39-41] studied this spontaneous polymerisation of 1,2-dimethyl-5-vinylpyridinium methyl sulphate (1,2-DM-5-VPMS), 1-methyl-2-vinylpyridinium methyl sulphate (1-M-2-VPMS), and 1-methyl-4-vinylpyridinium methyl sulphate (1-M-4-VPMS) in water:



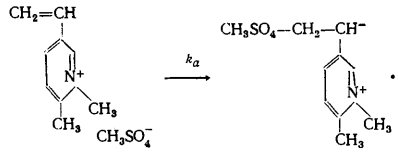
1,2-DM-5-VPMS 1-M-2-VPMS 1-M-4-VPMS

It has been established that carbon dioxide, sodium bicarbonate (which is in equilibrium with carbon dioxide), and sulphur dioxide are powerful inhibitors of spontaneous polymerisation. This finding eliminates Shyluk's hypothesis[42] of radical initiation and is in good agreement with the specific anionic mechanism of the polymerisation of 4-VP salts in organic media proposed above. Inhibition can then be regarded as a result of the addition of carbon dioxide or sulphur dioxide to the active centre carbanion.

When these inhibitors are present or specially added, induction periods appear on the kinetic curves. Using 1,2-DM-5-VPMS as an example, it has been shown that the duration of the induction period τ is related to the rate of generation of active centres v_a by the following simple expression characteristic of strong inhibitors:

$$\tau = [\text{inhibitor}]/v_a . \qquad (2)$$

Hence there is a possibility of a direct measurement of v_a. It may be expected that the rate of formation of active centres by reactions of the type of reaction (IX) (see p. 77) will be higher the greater is the polarisation of the double bond in the quaternary salt molecule. Indeed the rates v_a determined from the experimental values of τ and calculated by Eqn. (2) proved to be higher by a factor of 3.5–4 for 1-M-2-VPMS and 1-M-4-VPMS than for 1,2-DM-5-VPMS (in the range 10–35°, k_a for 1,2-DM-5-VPMS varies from 2.8×10^{-7} to 4×10^{-7} min^{-1}). Using 1,2-DM-5-VPMS as an example, the initiation reaction has been shown to be of first order with respect to the monomer, which is in complete agreement with the type (IX) mechanism, i.e.



(IX')

At the same time the kinetic curves for polymerisation in concentrated aqueous solutions (2.5 M and higher) yield satisfactory straight lines when plotted in terms of the equation for first-order reactions (Fig. 2) up to conversions (q) close to one. This means that the overall reaction is also of first order with respect to the monomer. However, the initial rate of reaction $(dg/dt)_0$ falls sharply when the initial concentration of the monomer $[M]_0$ is reduced (Fig. 3), although for a usual first-order reaction this quantity should not be a function of $[M]_0$ at all. At the same time the characteristic viscosities (molecular weights) of the polymers formed were found to decrease appreciably (Fig. 3). The temperature variation of the rate of polymerisation and the molecular weight is also quite unusual. When the temperature is increased, the rate of polymerisation and the characteristic viscosity pass through a maximum (Figs. 4 and 5).

All the attempts to account for all the experimental data using the normal concepts of homogeneous kinetics were unsuccessful. However, the observed relations can be readily explained if it is assumed that in concentrated solutions of monomeric salts ordered aggregates ("labile seeds") are present, whose lifetimes are greater or at least comparable with the time required for chain formation, as happens in liquid crystals. A hypothetical structure of an ordered aggregate is shown in Fig. 6. With this arrangement of the species in the aggregate, the double bonds form "layers" stabilised by hydrophobic interaction. It is suggested that "organised" monomer molecules, which retain sufficient mobility, are readily polymerised when an active centre enters an ordered layer. The electrical

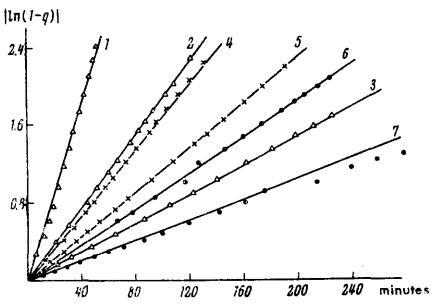


Fig. 2. Kinetic curves for the spontaneous polymerisation of vinylpyridinium salts plotted in terms of the equation for a first-order reaction:
1)–3) 1-methyl-4-vinylpyridinium methyl sulphate;
4) and 5) 1-methyl-2-vinylpyridinium methyl sulphate;
6) and 7) 1,2-dimethyl-5-vinylpyridinium methyl sulphate;
monomer concentrations (M): 1)–3) 3.5; 4) and 5) 4; 6) 3; 7) 2.5;
polymerisation temperatures: 1) 40°; 2), 6), and 7) 25°; 3) and 5) 35°; 4) 30°.

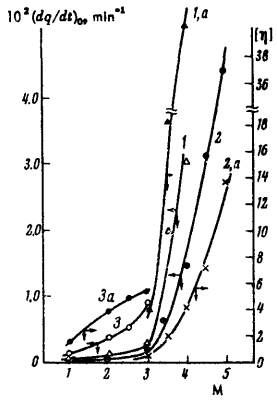


Fig. 3. Variation of the initial rate of polymerisation of vinylpyridinium salts and of the characteristic viscosity of the resulting polymers with monomer concentration: 1) and 1*a*) 1-methyl-4-vinylpyridinium methyl sulphate; 2) and 2*a*) 1-methyl-2-vinylpyridinium methyl sulphate; 3) and 3*a*) 1,2-dimethyl-5-vinylpyridinium methyl sulphate: temperature 25°; the viscosities were measured in 0.05 *N* aqueous solutions of potassium bromide.

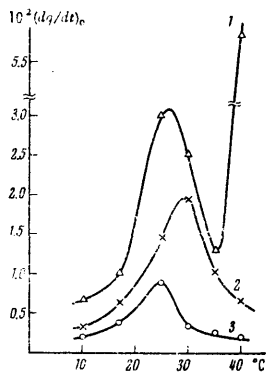


Fig. 4. Temperature variation of the initial rate of polymerisation of vinylpyridinium salts: 1) 4 M 1-methyl-4-vinylpyridinium methyl sulphate; 2) 4 M 1-methyl-2-vinylpyridinium methyl sulphate; 3) 3 M 1,2-dimethyl-5-vinylpyridinium methyl sulphate.

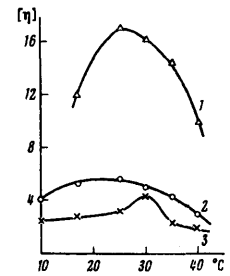


Fig. 5. Variation of the characteristic viscosity of polyvinylpyridinium salts with polymerisation temperature; the reaction conditions and the legend are the same as for Fig. 4.

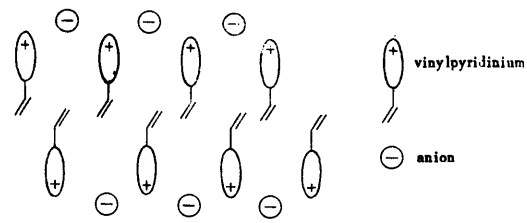


Fig. 6. The hypothetical structure of an organised aggregate in concentrated aqueous solutions of a vinylpyridinium salt.

double layer prevents the access of charged species, in particular H_3O^+ ions, to the growing chain and hence the destruction of carbanions by the addition of protons. Therefore the rate of polymerisation is independent of the pH of the medium between 2 and 9. In contrast to protons, the uncharged carbon dioxide and sulphur dioxide molecules easily reach the active centres and inhibit the process.

On the basis of the independence of the molecular weight of the degree of conversion (which has been shown experimentally and is evidence of the attainment of a steady state), the expression for the rate of polymerisation can be written in the form

$$-\frac{d[M]}{dt} = v_i\bar{\nu}, \qquad (3)$$

where [M] is the concentration of the monomer at any instant, $\bar{\nu}$ the average length of the kinetic chain, and v_i the rate of initiation. The first order of the initiation reaction with respect to the monomer, found experimentally, implies that

$$v_i = \varphi v_a = \varphi k_a[M], \qquad (4)$$

where k_a is the rate constant for the generation of active centres by a reaction of type (IX′) and φ is the initiation efficiency.

Noting that $q = (M_0 - M)/M_0$ and substituting Eqn. (4) in Eqn. (3), we obtain

$$\frac{dq}{dt} = \bar{\nu}\varphi k_a(1-q). \qquad (5)$$

At high values of $[M]_0$ the experimental variation of q with time is described by the equation

$$-\ln(1-q) = \bar{\nu}\varphi k_a t, \qquad (6)$$

which is obtained by integrating Eqn. (5). If it is assumed that, having attained the boundary of the ordered aggregate the active centre is immediately destroyed by combining with a proton or a water molecule, $\bar{\nu}$ should of course be related to the size of the ordered aggregates. In highly concentrated systems the formation of a macromolecule does not result in the breakdown of adjacent ordered regions.

Therefore $\bar{\nu}$ is independent of the degree of conversion ($\bar{\nu}$ = = const) and the polymerisation kinetics are described by the usual first-order equation. However, dilution of the initial system or a fairly appreciable temperature rise result in a decrease of the size of the ordered regions ("fusion") and the experimentally observed fall of the rate and the molecular weight. The validity of these considerations is confirmed by the sharp decrease of the viscosity of 1,2-DM--5-VPMS solutions on dilution (Fig. 7) and on raising the temperature, which is observed in the same range of concentrations and temperatures as the decrease of the rate and the molecular weight.

One of the causes of the increase of the rate with temperature in the region of lower temperatures must be attributed to the positive temperature coefficient of the initiation reaction ($E_a \simeq 7$ kcal mole^{-1} for 1,2-DM-5-VPMS). Thus the maxima on the rate–temperature curves can be explained by the superposition of two opposed factors — the increase of the rate of initiation and the breakdown of "labile seeds". However, this explanation cannot account for the extremal temperature variation of the molecular weight. Nevertheless, if it is assumed that chain termination occurs not only at the boundaries of the ordered aggregates but also, with a certain probability, within them (for example at water molecules which sometimes penetrate into the hydrophobic regions), then the extremal temperature variation of the molecular weight can also be satisfactorily accounted for. Indeed the maximum average length of the chains which can form under the given conditions ($\bar{\nu}_{max}$) is determined by the average length of the seeds. In the absence of chain transfer, the number-average degree of polymerisation $\overline{DP}$ can be expressed by the formula

$$\overline{DP} = (1-\lambda)\,\bar{\nu}_{max} + \lambda\,\frac{k_p}{k_t}, \qquad (7)$$

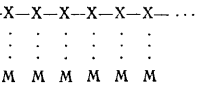
where k_p is the chain growth rate constant, k_t the chain termination rate constant within the seed, and λ the fraction of chains which are destroyed before reaching the end of the seed. If the activation energy for chain growth is higher than for chain termination within the seed, then at low temperatures most of the chains are terminated within the seeds ($\lambda \simeq 1$) and $\overline{DP}$ is determined by the ratio k_p/k_t and its temperature variation by the difference between the activation energies for chain growth and termination. In this temperature range $\overline{DP}$ increases with temperature. At high temperatures, where "fusion" takes place and the size of the ordered aggregates decreases, $\bar{\nu}_{max}$ falls and becomes smaller than k_p/k_t. Then most of the chains are destroyed at the edges of the seeds ($\lambda \simeq 0$) and $\overline{DP}$ is determined by the greatly reduced value of $\bar{\nu}_{max}$. In the absence of chain transfer, the rate of polymerisation can be written

$$-\frac{d[M]}{dt} = v_i\left[(1-\lambda)\,\bar{\nu}_{max} + \lambda\,\frac{k_p}{k_t}\right]. \qquad (8)$$

This expression explains the experimentally observed similarity of the variation of the rate of polymerisation and the molecular weight with the reaction conditions§.

Thus the concept of chemical activation of the monomer as a result of an intramolecular effect (polarisation of the double bond in the quaternary salt molecule) proved to be inadequate to account for the relations observed in the spontaneous polymerisation of vinylpyridinium salts in concentrated aqueous solutions. The kinetic data require the additional hypothesis of "labile seeds" which arise as a result of intermolecular interaction in the reaction system, i.e. of an intermolecular effect.

The combination of intra- and inter-molecular effects in chemical activation is closely related to the problem of "matrix" polymerisation. Suppose that the activator species X are chemically bound into long sequences. Then on addition of the monomer, the following system forms:



The monomer and the "matrix" can be chosen so that the reactivity of the monomer M bound to X should be significantly higher than that of free M. Then a chain M_n is formed from activated monomer molecules on each X_n sequence.

The reaction described recently by Furukawa and coworkers[43] may be quoted as an interesting example. In their study of the interaction between acetaldehyde and activated alumina the Japanese investigators observed that the adsorbed monomer polymerises with high yields at -70° to amorphous rubberlike polyacetal. The infrared spectrum of acetaldehyde adsorbed on alumina shows a pronounced bathochromic shift of the absorption band due to the carbonyl group, compared with the liquid monomer (6.4 instead of 5.8 μm), which indicates appreciable polarisation of the C=O bond (intramolecular effect). The authors[43] suggest that on adsorption the acetaldehyde molecules assume an ordered arrangement in the adsorption layer, as shown in Fig. 8 (intermolecular effect). Both factors favour rapid growth of polymeric chains, i.e. lead to the activation of the molecule.

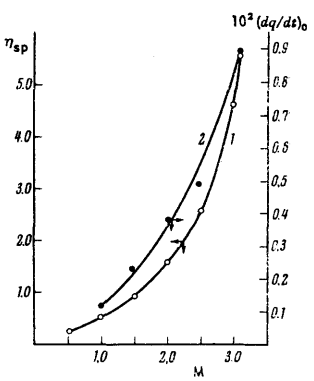


Fig. 7. Variation of the specific viscosity of an aqueous solution (curve 1) and the rate of polymerisation (curve 2) of 1,2-dimethyl--5-vinylpyridinium methyl sulphate with monomer concentration; the viscometric and kinetic measurements were made at 25°.

§ The behaviour of 1-M-4-VPMS in the temperature range 35–40° is exceptional (Fig. 4). Despite the continuing fall of the molecular weight, the rate of polymerisation increases suddenly after passing through a maximum by a factor of nearly six, which corresponds to an effective activation energy of about 70 kcal × × mole^{-1}. As before, the kinetic curves for polymerisation at 40° yield straight lines when plotted in terms of the equation for a first-order reaction (Fig. 2, curve 1). This effect can be attributed to a sudden rearrangement of the aggregates over a narrow temperature range.

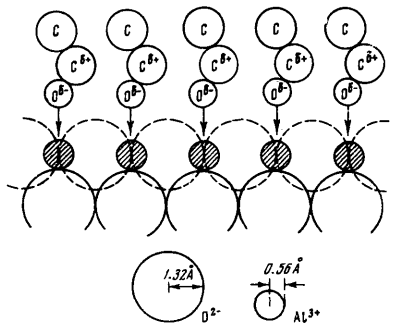


Fig. 8. Acetaldehyde adsorbed on the surface of γ-alumina [43].

The phenomenon of chemical activation of the double bonds of 4-VP in its conversion to the quaternary salt, described above, recently enabled Kargin et al. to achieve polymerisation on macromolecular "matrices" [7,8,10,13,44]. Polystyrenesulphonic acid (PSSA), polyethylenesulphonic acid (PESA), and polyacrylic acid (PAA) were used as the matrices. In all cases an equivalent amount of 4-VP was chemisorbed on the polymeric acids, activated, and polymerised by the mechanism described above. The products were polymeric salts, paired macromolecules of the polymeric acid and polymeric base (Fig. 9). The 4-VP molecules for which there is no room on the "matrices" remain inactive and are not involved in the reaction.

If the degree of neutralisation of the polymeric acid (i.e. the degree of saturation of the "matrix") is close to unity, the polymerisation of 4-VP on the polymeric acids is rapid at room temperature even in dilute aqueous solutions, since the activated monomer species are grouped along the polymeric activator chains regardless of the average concentration. However, the rate of polymerisation greatly depends on the degree of saturation, increasing sharply when the latter approaches unity. The problem of the effect of the degree of saturation of the "matrix" on the rate of the process is cardinal, since it is directly related to the problem of the elucidation of the nature of the interaction between the substrate and activator.

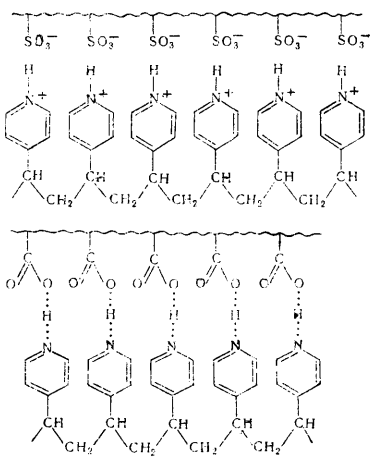


Fig. 9. The structure of the "matrix" polymerisation product.

The marked dependence of the rate of polymerisation on the degree of saturation α can be explained on two different hypotheses. The first of these reduces to the following. Suppose that the vinylpyridinium cations formed on neutralisation of the polymeric acid are firmly bound to its units and cannot migrate along the "matrix". The probability of the formation of a continuous sequence of p-activated 4-VP molecules is

$$\omega_p = \alpha^{p-1}(1-\alpha). \qquad (9)$$

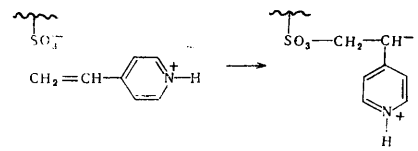
The average length of continuous sequences at a given value of α is

$$\bar{\nu} = \sum_1^\infty p\omega_p = \sum_1^\infty p\alpha^{p-1}(1-\alpha) = \frac{1}{1-\alpha}. \qquad (10)$$

If it is assumed that the length of the kinetic chain is determined by the length of the continuous sequence of activated molecules on the matrix, then, provided that initiation is possible in any unit of this sequence, the initial rate of polymerisation is

$$v_p = v_i\frac{\bar{\nu}}{2} = \frac{v_i}{2(1-\alpha)}, \qquad (11)$$

where v_i is the rate of initiation. Assuming further that the initiation reaction is of first order with respect to the monomer (see above), i.e. takes place by the mechanism



(XXIV)

one can write

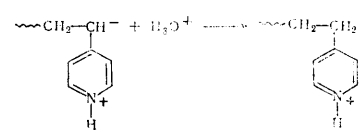
$$v_i = k_i[M] = k_i\alpha[C], \qquad (12)$$

where k_i is the initiation rate constant, [M] the concentration of the monomer, and [C] the concentration of the polymeric acid. On substituting Eqn. (12) in Eqn. (11), we obtain

$$v_p = {}^1/_2 k_i[C]\frac{\alpha}{1-\alpha}. \qquad (13)$$

Eqn. (13) predicts a rapid increase of the initial rate of polymerisation as α approaches unity (v_p tends to infinity when α = 1 because of the simplifying assumption made in the derivation that the "matrices" are of infinite length).

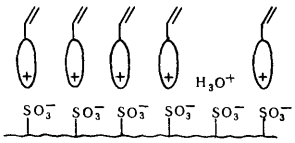
The second possible explanation is based on the assumption that activated 4-VP molecules can migrate within a certain space along the "matrix" and that the length of the kinetic chain for $\alpha < 1$ is related to the probability of the destruction of the active centre by the non-titrated hydronium ions, by the mechanism



(XXV)

In fact the "structure" of the reaction system formed on titration of the polymeric acid with 4-VP cannot ensure

electrostatic protection of the active centre from the non-titrated protons, in contrast to the mechanism adopted for the polymerisation of vinylpyridinium salts in concentrated aqueous solutions (see p. 81). This structure can be represented as follows:



(XXVI)

In the regions where the matrix is not saturated by the monomer, the probability of an encounter between an active centre and hydronium ions, which are held in the vicinity of such regions by the electrostatic interaction with the polymeric anion, is very high. Then the rate of chain termination v_t is given by the equation

$$v_t = k_t n [H_3O^+], \quad (14)$$

where k_t is the termination rate constant and n the concentration of active centres.

The average length of the kinetic chain at low conversions, when the change in the concentration of the activated monomer may be neglected, is given by the expression

$$\bar{\nu} = \frac{k_p n [M]}{k_t n [H_3O^+]} = \frac{k_p \alpha [C]}{k_t [H_3O^+]}. \quad (15)$$

The initial rate of polymerisation is

$$v_p = v_i \bar{\nu} = \frac{k_i k_p}{k_t} C^2 \frac{\alpha^2}{[H_3O^+]}, \quad (16)$$

where k_p is the chain propagation rate constant. Noting that for a strong acid

$$\alpha = \frac{[H_3O^+]_0 - [H_3O^+]}{[H_3O^+]_0},$$

where $[H_3O^+]_0$ is the concentration of hydronium ions in the non-titrated acid, we have finally

$$v_p = \frac{k_i k_p \alpha^2 [C]}{k_t (1 - \alpha)}. \quad (17)$$

Eqn. (17), like Eqn. (13), predicts a very rapid increase in the initial rate of polymerisation when α tends to unity.

In order to decide which of the two hypotheses is correct, it is necessary to "spoil" the "matrices" by titrating them before the addition of 4-VP with any non-polymerisable base, for example alkali. Then if we denote the degree of preliminary neutralisation by β and the overall degree of neutralisation by α as before, Eqn. (13) becomes

$$v_p = {}^1/_2 k_i [C] \frac{\alpha - \beta}{1 - (\alpha - \beta)}, \quad (13')$$

and Eqn. (17) becomes

$$v_p = \frac{k_i k_p (\alpha - \beta)^2 [C]}{k_t (1 - \alpha)}. \quad (17')$$

It follows from Eqns. (13′) and (17′) that the hypothesis of the rigid fixation of vinylpyridinium ions on the polymeric acid macromolecules leads to the theoretical prediction of a higher sensitivity of the rate of reaction to preliminary neutralisation in the range of α values close to unity than the hypothesis of chain termination by hydronium ions.

To decide which of the two kinetic equations describes the real process, two series of experiments were made. In the first series a 0.0119 N aqueous solution of PESA was titrated with 0.076 N aqueous solution of 4-VP to pH 5.6, which corresponds to $\alpha \simeq 0.999$. In the second series the same PESA solution was 50% titrated with the sodium hydroxide solution and then the pH was again brought to 5.6 by the addition of a solution of 4-VP. Thus in the first series of experiments we have $\beta = 0$ and $\alpha = 0.999$ and in the second series $\beta = 0.5$ and $\alpha = 0.999$. The rate of polymerisation was measured spectrophotometrically. It was found that in the solutions where $\beta = 0$ the rate of reaction was 3.6–3.9 times higher than in the solutions where $\beta = 0.5$.

It is now necessary to compare the result with the theoretical predictions. The relative decrease of the rate of polymerisation γ' on the assumption of rigid fixation of the activated monomers can be found by dividing Eqn. (13) by Eqn. (13′):

$$\gamma' = \frac{\alpha (1 - \alpha + \beta)}{(1 - \alpha)(\alpha - \beta)}. \quad (18)$$

On substituting the values of α and β specified in the experiments, we obtain $\gamma' \simeq 1000$, i.e. the rate of polymerisation on the "spoiled matrix" should be lower by a factor of one thousand than on the matrix titrated with 4-VP only. The relative decrease of the rate of polymerisation γ'' on the assumption of migration of vinylpyridinium ions along the polymeric acid molecules and the destruction of active centres by non-titrated protons is obtained by dividing Eqn. (17) by Eqn. (17′):

$$\gamma'' = \frac{\alpha^2}{(\alpha - \beta)^2}. \quad (19)$$

For the values of α and β used, $\gamma'' \simeq 4$, which is in good agreement with experiment.

It is striking that the morphology of the polymerisation products of 4-VP on polymeric acids is closely related to the form of the "matrix" in solution. Electron microscope studies have shown that in the polymerisation in methanol, where the macromolecules are rolled into globules, the polymeric salts form as disordered globular aggregates. In the polymerisation in water, where the matrices are ionised and extended, distinctly fibrillar structures are produced[7,8,10,13]. Thus chemical activation of 4-VP by polymeric acids is indeed due to a combination of intramolecular and intermolecular effects. It must be emphasised that the conversion of 4-VP into vinylpyridinium ions is by itself insufficient to ensure appreciable reaction rates in aqueous media. In dilute aqueous solutions of 4-VP salts and low-molecular acids there is virtually no spontaneous polymerisation. In equimolar mixtures of 4-VP and glacial acetic acid only traces of a polymer are formed in several days. At the same time 50% conversion of the 4-VP salt and PAA into a polymeric salt in 0.092 N solution at 20–50° is attained in 35–3 min (overall activation energy 26.4 kcal mole^{-1}). It may be supposed that in this case too the formation of "labile seeds" from activated monomeric molecules plays a very significant role, since it is difficult to account for the observed acceleration on going from low-molecular to high-molecular activators by the concentration effect alone.

Polymerisation on macromolecular activators still constitutes only a very rough approximation to the synthesis of polymeric chains in living cells. However, it is well known that preliminary chemical activation of the substrate is one of the fundamental principles of biochemical processes.

5. CHEMICAL ACTIVATION IN RADICAL POLYMERISATION

It is known that the properties of free radicals and the rates of radical reactions depend relatively little on the properties of the medium (in particular its polarity). However, this is true only in those cases where the species of the medium are incapable of specific chemical or semichemical interaction with the reacting species. Even relatively weak chemical interaction of the functional groups of the radical or monomer with the medium influences the chain growth rate constants in radical processes.

A systematic study of the role of organic complex-forming agents in radical copolymerisation was recently undertaken by Ryabov, Semchikov, and coworkers[45]. They showed, in particular, that introduction of proton donors into the system styrene (St)–2-VP alters markedly the composition of the copolymers formed on radical initiation, and, what is particularly important, the nature of the composition curves. Table 2 presents the relative activities and their products for the copolymerisation of styrene and 2-VP in the presence of various proton donors taken in ratios of approximately 1 : 1.5 relative to 2-VP. The table also gives the pK values of the complex-forming agents investigated.

In their solid-phase copolymerisation styrene and 2-VP do not exhibit a tendency towards alternation. Over the entire range of relative concentrations the copolymer is slightly enriched in 2-VP. In the presence of proton donors a tendency towards alternation appears, and increases with the acidity of the donor. The authors attribute the observed effect to the positive polarisation of the double bond in the 2-VP molecule, as a result of the formation of a hydrogen bond between the nitrogen atom of the pyridine ring and the complex-forming agent. This conclusion is confirmed to some extent by the application of the Hammett equation and the Q–e scheme to the data obtained.

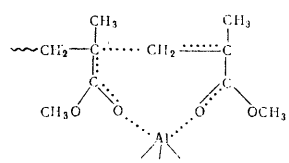
Strong inorganic complex-forming agents have an even more significant influence on radical polymerisation. In 1958 Bamford et al.[46] showed that the rate of polymerisation of acrylonitrile (AN) in dimethylformamide, initiated by free radicals, increases appreciably on addition to the system of lithium chloride which forms complexes with C≡N groups. A preliminary explanation of this effect was based on the postulated higher reactivity of the complexed chain propagation radicals. Two years later Kargin et al.[47] noted that the rate of the photo-initiated polymerisation of methyl methacrylate (MMA) saturated with zinc chloride increases sharply near the interface between the crystals and the liquid. At the same time Parrot and Monteiro[48] confirmed the results of Bamford and coworkers[46] by their observation of the acceleration of the radical polymerisation of acrylonitrile on addition of lithium chloride, magnesium chloride, and aluminium chloride. Data on the effect of zinc chloride on the polymerisation kinetics and the copolymerisation rate constants for a number of monomers were obtained by Imoto and coworkers[49]. The kinetic measurements of Bamford and coworkers[50] showed that the acceleration of photopolymerisation in the system MMA–$ZnCl_2$ is due to an increase of the chain propagation rate constant: the chain termination rate constant remains virtually unchanged.

TABLE 2. Effect of organic complex-forming agents on the copolymerisation constant of styrene (M_1) and 2-vinylpyridine (M_2).[45]

Complex-forming agent	pK	r_1	r_2	$r_1 \times r_2$
—	—	0.57 ±0.05	1.33 ±0.08	0.758
Ethanol	18	0.486±0.07	0.862±0.08	0.418
Methanol	16	0.426±0.05	0.607±0.06	0.258
Phenol	9.95	0.253±0.06	0.549±0.07	0.139
Acetic acid	4.75	0.16 ±0.04	0.36 ±0.07	0.058

The problem of the mechanisms leading to an increase of the rate of the radical-initiated chain propagation in the presence of inorganic complex-forming agents is at present the subject of detailed studies. The first attempt at a theoretical interpretation of this phenomenon was undertaken by Tazuke et al.[51] by the molecular orbital method. Using the simple LCAO approximation, they calculated the values for the extent of delocalisation S_r^R, regarded as a measure of the reactivity of the monomer, and of the stabilisation energy of the transition state ΔE_{rs} for complexes of various substituted derivatives of vinylpyridine, acrylonitrile, and methyl methacrylate with zinc chloride, and obtained a qualitative agreement between the theory and the kinetic experiments. Such calculations are made essentially to take into account the intramolecular effect of the complex-forming agents. However, in many cases chemical activation probably cannot be explained solely by the intramolecular effect, particularly in solid-phase polymerisation or in polymerisation in concentrated solutions in the presence of stoichiometric or nearly stoichiometric amounts of complex-forming agents.

Some light has been thrown on this problem by the results of Zubov et al.[52], who investigated the solid-phase photopolymerisation of methyl methacrylate in the presence of aluminium chloride and bromide. The kinetic data, the study of the infrared spectra of the complexed monomer, and the ESR spectra of the complexed radicals enabled the authors to put forward certain ideas concerning the mechanism of the acceleration of the polymerisation. It is suggested that, in the presence of low concentrations of inorganic activators (i.e. for monomer : activator ratios significantly lower than the stoichiometric values), the observed acceleration is mainly caused by the intramolecular effect. The hypothetical structure of the activated complex may be represented as follows:



(XXVII)

The unpaired electron of the complex radical, which according to the ESR data spends some time on the aluminium atom (spin density on aluminium about 1%), is transferred to the monomer molecule in the transition state. It is suggested that this fundamental step has a higher probability than the usual radical addition. For this reason, the chain propagation rate constant is higher in the presence of the complex-forming agent. However, the above hypothesis cannot account for the kinetic data obtained when the monomer : complex-forming agent ratios are close to the stoichiometric value. In this case the formation of organised aggregates of complexed methyl methacrylate molecules ("labile seeds"), favouring chain growth, probably

begins to play a significant role, as happens, for example, in certain liquid crystals (intermolecular effect).

Quite recently Nechaev et al. [53] observed the acceleration of the photo-initiated polymerisation of methyl methacrylate in the presence of 4% oleum. It was found that the rate of polymerisation increases with the concentration of sulphuric acid and passes through a maximum. At the molar ratio H_2SO_4 : MMA = 1 the molecular weight is also a maximum (Fig. 10). It may be supposed that in this case the intermolecular effect is one of the causes of the chemical activation of methyl methacrylate.

The intramolecular effect postulates cannot account for the sharp increase in the rate of the radiation-induced photopolymerisation of allyl monomers in the presence of zinc chloride [52]. Allyl acetate (AA) to which an equimolar amount of zinc chloride has been added polymerises 5.5–6 times faster. The rate of polymerisation of allyl alcohol (AAlc) increases by a factor of 24 in the presence of zinc chloride at an allyl alcohol : zinc chloride ratio of 2. Since the double bond in allyl monomers and the unpaired electrons in the corresponding chain propagation radicals are not conjugated with the functional groups participating in the formation of complexes, it is difficult to expect an appreciable change in their reactivity as a result of the addition of zinc chloride. One of the possibilities consists in the activation of the complexed allyl chain transfer radicals. Nevertheless this alone does not fully explain the observed kinetic features. The explanation should probably also be sought in a combination of intramolecular and intermolecular effects.

Radical polymerisation in the presence of complex-forming agents has been recently introduced in polymer chemistry and its further development will probably lead to fundamentally new methods for the control of the rates and the stereochemistry of radical processes. The studies of the chemical activation of monomers in the formation of charge-transfer complexes which have been begun in a number of laboratories are particularly promising.

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The problems of the polymerisation of chemically activated monomers may be regarded as part of the general problem of the effect of the interaction between the substrate and the species derived from the medium on the capacity of the substrate to undergo a particular reaction. The

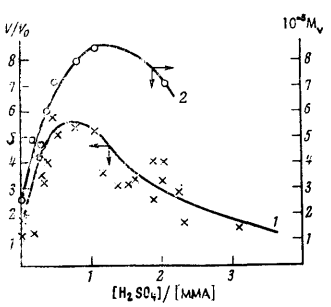


Fig. 10. Variation of the relative rate of polymerisation of methyl methacrylate (curve 1) and the molecular weight of the resulting polymer (curve 2) with the monomer : activator molar ratio at 20°.

averaging simplification associated with the introduction of the macroscopic concept (medium) is always to some extent a consequence of the insufficient knowledge of the investigator of the nature and distribution of the concrete interactions in the reaction system at a molecular level. This averaging simplification is very convenient in analysis and is probably justified in the case of weak interactions, but it involves fundamental limitations in the elucidation of the detailed mechanisms of chemical reactions. The present review deals with systems for which the necessity to formulate the term "interaction with the medium" in a more concrete form is quite evident. The examination of the monomer–activator problem on a somewhat wider scale leads to an important generalisation. Imagine a system in which the number of monomer molecules is somewhat higher than the number of activated molecules. If the activator combines with the units of the polymer being formed as strongly or more strongly than with the monomer molecules, then during the reaction the fraction of the activated monomer decreases continuously. Actually this means that in the initial system part of the less active monomer is replaced by a more active variety. Examples of such systems are quoted above. If the bond between the activator and the polymer chain units is much weaker than that with the monomer, then one activator molecule can be used repeatedly and can facilitate the polymerisation of a large number of monomer molecules: the concept of the "activator" merges with the classical concept of the "catalyst". An example is the polymerisation of *N*-carboxy-anhydrides examined above. Finally, if the activator molecules interact with the growing ends of the chain more strongly than with the average monomer molecules and with the macromolecular units, they will be retained at the end of the chain during its growth and, within the framework of the generally adopted interpretation of catalytic polymerisation processes, the activator may be regarded as a component of the catalytic complex responsible for the chain process. This is precisely what happens in the lithium-induced polymerisation of methyl methacrylate, dienes, etc. in the presence of organic donors (tetrahydrofuran, amines, etc.).

Between these three limiting cases enumerated above, there should be a multiplicity of intermediate situations. A number of deviations from the normal behaviour of catalysts are known. It cannot be excluded that such "deviations" should in fact be regarded as an effect of the general laws governing the characteristics of systems of an intermediate type.

The above discussion is applicable to a wide range of other chemical processes as well as polymerisation. Further progress in this field will probably lead to a general examination of the problem of catalysts, active solvents, modifiers, etc.

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THE STRAINED DOUBLE BOND

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I. INTRODUCTION

The problem of the dependence of the properties of compounds on the deformation of the angle between the bonds is being studied at present very intensively, both theoretically and experimentally; strained compounds such as bicyclobutane[1], diphenyltetrahedrane[2], cubane[3], and others have been synthesised successfully. Compounds with altered valence angles are characterised by an increased content of internal energy, which changes their physical and chemical properties. Thus the far-reaching analogy in the properties of cyclopropane and olefin derivatives is generally known.

The term "strain", introduced by Bayer[4] in 1885, does not explain the significance of the above processes, which are probably of widely different types. Usually it is understood to imply deformation of the valence angles and the associated deformation of the molecules. Since the angles between the orbitals† of the carbon atoms in various hybrid states are different, there is a possibility of representing certain changes in valence angles as a result of rehybridisation. An idea of this kind was applied for the first time in 1949 by Walsh[5] and also by Coulson and Moffitt[6] to account for the structure of cyclopropane. Nowadays this view has been widely adopted.

The strained double bond is of particular interest. All the substituents at a double bond are in the same plane as the olefinic carbon atoms; the normal C=C–X angle is assumed to be 120° (the angle between the orbitals of the sp^2 hybridised carbon atom[7]). Deviation from this geometry requires an expenditure of energy and the internal energy of molecules containing such a fragment is higher. In real compounds the C=C–X angle almost always differs from 120°, if only because of the breakdown of ideality due to different bond lengths[8] (in ethylene 117° 30'), but the deviation of both valence angles at the double bond by 5° causes an energy increase of only 1 kcal mole^{-1}. Since the concept of strain is largely qualitative, we shall regard a double bond as "strained" when the deviation from the "ideal" geometry is so great that it begins to have an effect on the physical and chemical properties of the compounds containing the given fragment.

A considerable number of original studies dealing with the strained double bond have appeared recently in the literature. However, this problem has not been examined as a whole, and the aim of the present review is to fill this gap.

II. TYPES OF STRAIN IN THE DOUBLE BOND

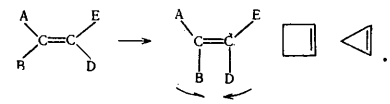
From the formal point of view, the decrease of the valence angle between two bonds of a tetragonal atom can cause the atom to become "olefin-like"; according to Bayer's theory, the double bond may be regarded as a two-membered ring (this description of the double bond is still used, but to a lesser extent than the σ,π-method[8-10]).

In contrast to the tetrahedral atom, strain in the double bond can occur in different ways, which are non-equivalent as regards the induced rehybridisation of the olefinic carbon atom; these will therefore be considered separately.

If the double bond has four substituents A, B, D, and E, then all types of strain in the double bond can be divided into two groups: those occurring in the ABDE plane and those involving the displacement of any one substituent from this plane.

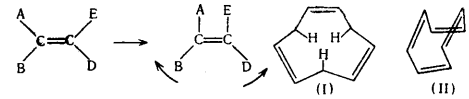
1. Deformation in the Plane of the Double Bond

The deformation of the valence angles in the plane of the double bond (ABDE) can in turn occur in several ways. One of the possibilities is the decrease of the valence angle as a result of the mutual approach of the groups B and D in the *cis*-position ("cisoid compressive strain"):



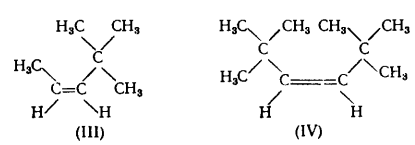
Such strain occurs, for example, in cyclo-olefins with small rings — in cyclobutene or cyclopropene. These examples show that the deformation of the valence angles (considered from a formal standpoint) can become very high. Thus the deviation of the C=C–C valence angle from the normal value in cyclobutene[11] is 26° 06' and in cyclopropene[12] 55° 24'. From the point of view of structural theory, cisoid compressive strain should result in more "acetylenic" character of the double bond; this was apparently foreseen by Bayer[4]. Nowadays it is assumed that such strain should lead to rehybridisation of the olefinic atoms with increase of the *s*-character of the exocyclic bonds (C–H bonds of unsubstituted monocyclic olefins) and the *p*-character of the endocyclic C–C bonds. It is interesting that also from the point of view of Walsh's model of cyclopropene[5] there should be a definite analogy in the properties of acetylene and cyclopropene. Attention will be drawn to this analogy in the properties of strained olefins with cisoid compressive strain and acetylenes in further discussion below.

Another type of strain is the increase in valence angles as a result of the repulsion of the groups B and D in *cis*-position ("cisoid repulsion strain"):



(I) (II)

It would appear that this type of strain should occur in macrocyclic olefins. However, the latter are non-planar and the valence angles are very close to the normal value. Nevertheless in cyclohexene[13,14] the C=C–C angle is already 122°, i.e. slightly higher than the normal value. The increase of the valence angle and hence the strain in the double bond is influenced by the transannular repulsion of hydrogen atoms in cyclic olefins. For example, the C=C–C angle in *cis,cis,cis*-cyclononatriene (I)[15-17] is 124°, due to the repulsion of the mutually non-bonded hydrogen atoms. Cisoid repulsion strain occurs also in cyclo-octatetraene (II), where the C=C–C angle is 126° 46'.[18] The cisoid increase of valence angles can also take place in non-cyclic compounds. An example of this kind is *cis*-t-butylmethylethylene (III)[19] and *cis*-di-t-butylethylene (IV)[19,20]:



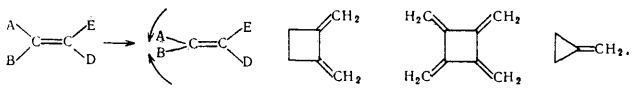
(III) (IV)

† This terminology is used in accordance with the recommendation of the Second Conference on Quantum Chemistry (Vilna, 1962).

Although there are no literature data for the valence angles in compounds (III) and (IV), measurements of the heats of hydrogenation (see below) undoubtedly indicate a considerable strain of the double bond in compound (III) and particularly (IV).

In the case of cisoid repulsion strain rehybridisation with increase of the *s*-character of the endocyclic bonds and the *p*-character of the exocyclic bonds [in compounds (I)–(IV) these are C–H bonds] should also occur and therefore the changes in bond character should be the opposite of those observed for cisoid compressive strain.

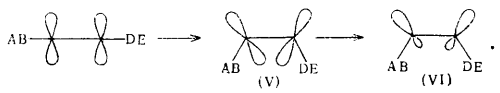
Further, there is a possibility of "unilateral compressive strain" of the double bond in the ABDE plane as a result of the mutual approach of groups A and B:



This type of strain occurs, for example, in dimethylenecyclobutane[21], tetramethylenecyclobutane[22], and methylenecyclopropane[23] molecules. Evidently repulsion strain of this type can also exist in the presence of two bulky groups at one of the carbon atoms of the double bond.

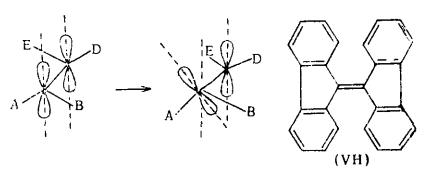
2. Deformation of the Double Bond with Displacement of the Substituents from a Single Plane

The strain of the double bond involving the displacement of the substituents from the ABDE plane can also occur in several ways. Strain in the double bond with displacement of all four substituents below the plane of the double bond ("out-of-plane strain") is possible:



The transition (V) → (VI) should then occur[24]. This is due to the tendency of the olefinic carbon atom to undergo a transition from the sp^2-hybridised state to the sp^3-hybridised state in the presence of such deformation of valence angle. However, examples of compounds of this type are evidently so far unknown. It is also noteworthy that this type of strain in the double bond is to some extent analogous to that in compounds of the type of dehydrobenzene[25].

Another type of strain in the double bond involving the displacement of the substituents from the plane of the double bond is "torsional strain":

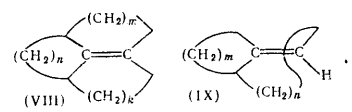


Rotation about the double bond entails a decrease of the degree of overlap of *p*-electrons, which is approximately proportional to the square of the cosine of the angle of rotation[7,26]. Dibiphenylene-ethylene‡ (VII) can serve as an example of a compound with torsional strain; in this case the rotation is due to the repulsion of the mutually non-bonded hydrogen atoms in the *peri*-positions. According to Rummens[27], torsional strain cannot be compensated by rehybridisation.

It is noteworthy that torsional strain causes a much greater increase in the energy of the ground state than in the energy of the excited state. This can be illustrated by the results of the calculation of Coulson and Jacobs[28] which show that the order of the double bond in stilbene in the ground state is 1.820 and in the first excited state only 1.436; therefore the difference between the energies of these states should decrease with increase in torsional strain. For the ground N-state of ethylene, rotation by 90° requires the expenditure of 61 kcal mole^{-1}.[29,30]

Thus strain in the double bond can occur in different ways and sometimes it is difficult to decide to which type of strain a particular case should be assigned. In this respect, *trans*-cyclo-octene is interesting. In early studies it was assumed that the double bond fragment in this compound is planar and that the strain in the molecule is due to the deviation of the valence angles from the normal value[31]. However, in subsequent studies involving the investigation of the dipole moment and the infrared spectrum[24] of *trans*-cyclo-octene and also its separation into optical isomers[32,33] it was assumed that torsional strain occurs in this compound and the angle of rotation was estimated[34] as 17° ± 5°.

In addition, in complex polycyclic systems there is a possibility of cases involving the combination of certain types of strain of the double bond, as, for example, in the hypothetical structures (VIII) and (IX):



III. ESTIMATE OF THE STRAIN IN THE DOUBLE BOND

In many calculations of the conformations of cyclic compounds[35–40] and solvolytic reactivity[39,40] it has been shown that the deformation of the angle between the bonds is not localised but extends to other bonds, so that the energy of the system as a whole is a minimum. Therefore, there is no doubt that the deformation of the angle at the double bond entails a certain deformation of the remaining angles. However, as an approximation the overall strain may be regarded as the sum of the different types of strain [angular strain, bond extension, torsional (Pitzer) strain, interaction between mutually non-bonded atoms[41]] and therefore in favourable cases one may speak of the intrinsic strain of the double bond.

The strain can be estimated experimentally from thermochemical data[42]. Thus comparison of the negative heats of hydrogenation of cyclohexene (27.1 kcal mole^{-1})[43] with those of *cis*- and *trans*-but-2-enes (28.5 and 27.5 kcal × × mole^{-1} respectively)[44] shows that the double bond in cyclohexene is unstrained. The heats of hydrogenation of cyclo-olefins are presented in Table 1. In comparing these data, account must be taken of the fact that they may have been obtained under different conditions; however, the error does not exceed 1 kcal mole^{-1}.[42,45]

The negative heat of hydrogenation of compounds with cisoid compressive strain increases with decrease in ring size and is a maximum in cyclopropene[46] (53.9 kcal mole^{-1}).

‡ Better termed 9,9′-bi(fluorenylidene) (Ed. of Translation)].

TABLE 1. Estimate of the double bond strain in certain cyclo--olefins.

Ring size	Excess strain of cycloalkane (Ref. 57) E_{strain}, kcal mole^{-1}	ΔH_{hydr}, kcal × × mole^{-1}	Excess strain of cycloolefin E_{strain}, kcal mole^{-1}	C=C–C angle in cyclo-olefin	Double bond strain [$(E_{strain}$(double bond)], kcal mole^{-1}	
					calc. from angle by Eqn. (1)	calc. from thermochemical data
C_3	27.6	53.9 [46]	54.3	64°36′ [12]	107.4	45.1
C_4	26.2	—	—	93°54′ [11]	23.8	—
C_5	6.1 *	26.9 [58]	5.9	111°30′ [60]	2.5	2.3
C_6	0	27.1 [13]	0	122°30′ [14]	0.2	0
C_7	6.4	25.9 [48]	5.2	—	—	0.7
C_8 *cis*	9.9	23.0 [59]	5.8	—	—	—
C_8 *trans*		32.2 [59]	15.0	—	—	9.2
C_9 *cis*	12.9	23.6 [59]	9.4	—	—	—
C_9 *trans*		26.5 [59]	12 3	—	—	2.9
C_{10} *cis*	12	20.7 [59]	6.6	—	—	—
C_{10} *trans*		24.0 [59]	8.9	—	—	3.3
Norbornane XIV	13	33.1 [45]	19	109° [55]	4.2	>6

* Calculated from ΔH°_{form},[44] taking E_{C-H} = 98.7 kcal mole^{-1} and E_{C-C} = 82.6 kcal mole^{-1}.[45]

The double bond in bicyclic bridged systems is also strained. Table 1 shows that the negative heat of hydrogenation of norbornene (X) is very considerable. Similarly $-\Delta H_{hydr}$ for bicyclo[2,2,2]octene[43] (XI) is 28.25 kcal mole^{-1}, that for the first double bond in norbornadiene[43] (XII) is 35 kcal mole^{-1} and that for the first double bond of barrelene[47] (XIII) is as much as 37.6 kcal mole^{-1}.



(X) (XI) (XII) (XIII) (XIV)

Compounds with cisoid repulsion strain can also be considerably strained. Thus the negative heat of hydrogenation of *cis*-t-butylmethylethylene (III) is 30.8 kcal mole^{-1} and that of *cis*-di-t-butylethylene[19] (IV) is 36.2 kcal mole^{-1}. The negative heats of hydrogenation of the *trans*-isomers of these olefins are 26.5 and 26.87 kcal mole^{-1} respectively, i.e. close to the value for the unstrained double bond.

However, direct comparison of the heats of hydrogenation cannot always be used to estimate the strain of the double bond. In fact, the heat of hydrogenation characterises the difference between the heat contents of the olefin and the corresponding paraffin, i.e. the difference between their heats of formation. Therefore, the heat of hydrogenation depends not only on the strain of the double bond but also on the strain in the saturated hydrocarbon which obtains on hydrogenation: the greater the strain of the paraffin, the higher is its heat of formation and the lower the negative heat of hydrogenation. This is clearly seen in the heats of hydrogenation of cyclo-octene, cyclononene, and cyclodecene (Table 1). The decrease of the negative heat of hydrogenation is in this case due to the strain in the corresponding cycloparaffins[31]. Similarly the negative heat of hydrogenation of cyclopentene is lower than that of cyclohexene, despite the fact that the deformation of the double bond is higher in cyclopentene; the explanation is that the strain in cyclopentane is higher than in cyclohexane[48]. The excess strains in cycloparaffins relative to the unstrained cyclohexane are also given in Table 1.

Therefore, the strain of the double bond can be estimated directly from the heats of hydrogenation only when the saturated hydrocarbon is unstrained. Thus it follows from the above data that the strain of the double bond in compound (III) is equivalent to 4.3 kcal mole^{-1} and in compound (IV) to 9.9 kcal mole^{-1}. If the strain in the cycloparaffin is neglected, the lower limit to the strain of the double bond can be estimated. Thus the strain of the double bond in norbornene should not be less than 6 kcal mole^{-1} and in *trans*--cyclo-octene it should not be less than 5.1 kcal mole^{-1}.

It is also possible to estimate the upper limit of the strain of the double bond by a different procedure. The overall strain in the cyclo-olefin relative to cyclohexene is[45]:

$$E_{strain}\,(\text{olefin}) = \Delta H_{hydr}\,(\text{olefin}) - \Delta H_{hydr}\,(\text{cyclohexene}) + E_{strain}\,(\text{paraffin}).$$

The values calculated for these conditions are presented in Table 1. The overall strain in the olefin [E_{strain}(olefin)] relative to cyclohexene includes the excess strain in the double bond and in other groups. The strain of the double bond can be estimated from data on the excess strain in the paraffin per CH_2 group. If it is assumed that this quantity is the same also for the olefin, then the strain of the double bond can be calculated thus:

$$E_{strain}\,(\text{double bond}) = E_{strain}\,(\text{olefin}) - (n-2)E_{CH_2}\,(\text{paraffin}).$$

The data for cyclopropene, cyclopentene, and cycloheptene calculated in this way are also listed in Table 1. Evidently the results represent the upper limit to the strain of the double bond. It is also clear that such calculation for *cis*-cyclo-octene and higher cyclo-olefins gives somewhat indefinite results, since the strain per CH_2 group in the cycloparaffin is significantly higher than in the *cis*--cyclo-olefin due to the transannular repulsion of hydrogen atoms.

Finally the strain of the double bond in *trans*-cyclo--olefins can be roughly estimated from a comparison of the heats of hydrogenation of the *cis*- and *trans*-isomers. For *trans*-cyclo-octene, such comparison yields 9.2 kcal × × mole^{-1}.

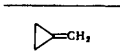
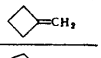
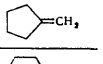
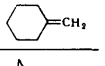
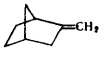
The energy which must be expended to cause the deviation of the valence angle from the normal value may be calculated[8,49] from the equation

$$E = \frac{1}{2}k\alpha^2, \qquad (1)$$

where k is the bending force constant and α the deviation of the angle from the normal value. A large number of semiempirical calculations of the strain energy and of the stable conformations of cycloparaffins have been made[35-38]. Eqn. (1) is also applicable to the calculation of the conformation and strain in cyclo-olefins. It is noteworthy that usually the force constant for the C=C–X angle is higher than that for the C–C–X angle[49,50], which shows that it is more difficult to alter the angle of the sp^2-hybridised atom. The conformation of cyclohexene was in fact calculated in this way[13,14]. The present authors calculated the double bond strain energy for certain cyclo-olefins, the results and the C=C–C angles being listed in Table 1. The bending force constant for the C=C–C angle was taken to be 0.8×10^{-11} erg radian^{-2}, i.e. close to the C–C–C force constant in cyclobutane[51] (for justification of this choice, see Ref. 49).

Critical examination of the limits of applicability of this method among cycloparaffins[49] shows that, whereas for cyclobutane the agreement with experiment is more or less

TABLE 2. Properties of hydrocarbons with unilateral double bond strain.

Substance	$-\Delta H_{hydr}$, kcal mole^{-1} (Ref.61)	Frequencies in the infrared spectra cm^{-1}		K_{eq} for Ag^+ complexes in ethylene glycol at 40° (Ref. 66), litre mole^{-1}
		C=CH$_2$ groups in olefins (Refs. 62 and 63)	C=O groups in corresponding ketones (Ref. 62)	
	—	1730	1815	—
	29.4	1679	1788	5.8
	26.9	1657	1746	4.0
	27.8	1651	1715	6.0
	—	1665 [64]	1751 [65]	4.3

satisfactory, for cyclopropane such calculation yields a strain energy which is much too high and therefore the method can be applied only in the case of small or at any rate moderate deformations of the valence angle. When the deformation of the angle is considerable, involving the formation of "banana" bonds [51-54], the above method of calculation cannot be used. Calculations on the cyclopropene molecule [12] show that, although formally the angle between the bonds in the methylene group of cyclopropene is 50°48', the angle between the orbitals is 105° 35' and therefore "banana" bonds are formed in this case. Table 1 also shows that the calculated value of 109° for the angle in norbornene [55,56] is somewhat too high and therefore the strain of the double bond should be greater. This finding is also confirmed by spectroscopic data (see below).

The application of Eqn. (1) to *cis*-di-t-butylethylene (IV), taking into account the strain of the double bond, permits the calculation of the C=C–C angle in this compound, which is found to be 136°.

Finally, the published data on the heats of hydrogenation of certain compounds with unilateral compressive strain (Table 2) show that the strain of the double bond in methylenecyclobutane is not less than 1.6 kcal mole^{-1}, but it is evident that this value is significantly too low because of the strong repulsion of the mutually non-bonded hydrogen atoms and the methyl group in methylcyclobutane. Nevertheless the strain of this bond is smaller than would be expected from the valence angles in this compound.

IV. PHYSICAL PROPERTIES OF THE STRAINED DOUBLE BOND

From the formal point of view, the decrease of the angle between the bonds of the tetragonal carbon atom results in the atom becoming increasingly more "olefin-like". This was probably suggested by Bayer: it is not fortuitous that he examined the problems of the theory of strain in an article dealing with unsaturated compounds [4]. Formally, it is possible to calculate the "strain" in the formation of the double and triple bond in the same way as for cycloparaffins [4,10].

Similarly cisoid compressive strain should cause the bond to acquire "acetylenic character" and, as already stated above, there should be an analogy between olefins with cisoid compressive strain and acetylenes. Such analogy should undoubtedly be reflected in the physical properties of olefins of this type. However, as mentioned above, different types of strain of the double bond may be non-equivalent from the standpoint of the possibility of the compensation of the strain by rehybridisation and therefore strained olefins can exhibit significantly different relations in their physical properties.

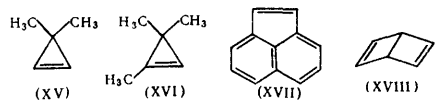
1. Nuclear Magnetic Resonance Spectra

As already stated, compounds with cisoid compressive strain should show an increase of the *s*-character of the exocyclic bond. In recent years estimates of the fractional *s*-character of the C–H bond from the spin–spin interaction constant $J(^{13}C-H)$ have been made extensively. A simple relation was proposed in 1959: [67,68]

$$\% S = \frac{J(^{13}C-H)}{5}. \quad (2)$$

The value of $J(^{13}C-H)$ for the carbon–hydrogen bond of an sp^3-hybridised atom is about 125 c/s (125 c/s for methane [67], 123 c/s for cyclohexane [67]), and for acetylenic compounds it is about 250 c/s (248 c/s for methylacetylene [67], 251 c/s for phenylacetylene [67]). For unstrained olefins, $J(^{13}C-H)$ is in the region of 157 c/s (157 c/s for ethylene [69], 159 c/s for benzene [69], 155 c/s for cyclo-octatetraene [69]).

The values of $J(^{13}C-H)$ for certain cycloalkanes and cycloalkenes are presented in Table 3, which shows that $J(^{13}C-H)$ increases with the cisoid compressive strain. This may be attributed to the increase of the *s*-character of the =C–H bond with increasing strain in the double bond. The value of $J(^{13}C-H)$ for cyclopropene is unknown, but for 3,3-dimethylcyclopropene [70] (XV) and 2,3,3-trimethylcyclopropene [70] (XVI) these constants are 220 and 218 c/s respectively and thus the hybridisation of the carbon atoms at the double bonds in these compounds is significantly different from the hybridisation in ethylene.



(XV) (XVI) (XVII) (XVIII)

TABLE 3. Certain spectroscopic characteristics of cyclo-olefins.

Ring size	NMR spectra			Infrared spectra (cm^{-1})			λ_{max} for phenyl derivatives, nm	
	$J(^{13}C-H)$, c/s			C–H vibrations in cyclo-olefins				
	C–H in cycloalkane	=C–H in cycloalkene	chemical shift τ due to olefinic protons (Ref.62)	ν^{s}_{C-H}	ν^{as}_{C-H}	C=C vibrations	of type (XXV) (Refs. 98, 99)	of type (XXVI) (Ref. 100)
C_3	161 [93]	(220)***	2.99	3076 [62]	—	1641 [62]		308, 317****
C_4	134 [94]	170 [96]	4.03	3060 [83]	(3019)**	1570 [83]		297, 307
C_5	128 [67]	160 [69]	4.40	3060 [85] 3045 [97]	(3039)**	1615 [63]	254	272
C_6	124 [94,95]	157 [69]	4 41	3024 [62]	3067 [62]	1654 [63]	248	253
C_7	123 [94]		4.29	3020 [62]	3059 [62]	1650 [62]	247	254
C_8 *cis*			4.44	3010 [24]		1664 [24]		
C_8 *trans*	122 [94]			3016 [62] 3000 [24]	3053 [62]	1648 [62] 1658 [24]		
Norbornene (XIV)	(135)*	174 [69]	4.06	3070 [97]		1568 [97]	262	

* The value for protons at C_1 and C_4 in norbornadiene (XII). [94]
** Calculated value. [83,85]
*** Value for 3,3-dimethylcyclopropene (XV). [88]
**** Values for 3-hydroxymethyl-1,2-diphenylcyclopropene (XXVII).

The constants for norbornene (X)[69] (174 c/s), norbornadiene (XII)[71] (168 c/s), and acenaphthylene (XVII)[69] (178 c/s) also show that their double bonds are strained. Possibly the high strain of the double bond in acenaphthylene is in fact responsible for the high heat of polymerisation (24.0 kcal mole^{-1}) of this compound[45].

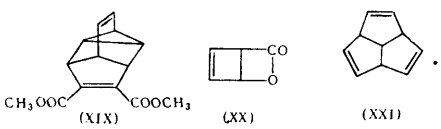
We may note that the above simple equation gives $J(^{13}C-H)$ = 166.5 c/s for the C–H bond of the sp^2-hybridised atom. Nevertheless the fractional s-character of many compounds has been calculated in this way. This procedure has been criticised[72,73]. It has been shown that in some cases (for example, for halogeno-derivatives) other factors exert a dominant effect[74]. Apparently, only when compounds with similar structures are compared is it possible to make fairly reliable conclusions on the basis of the variation of $J(^{13}C-H)$, provided that it is sufficiently pronounced. Here we must point out that so far $J(^{13}C-H)$ has been almost always determined from proton spectra. Burke and Lauterbur[75] compared the values obtained from proton and ^{13}C spectra for a number of cycloalkanes and found certain discrepancies (the greatest discrepancy was found for cyclodecane: 8 c/s). It is very interesting that their calculation confirmed that the observed values of $J(^{13}C-H)$ derived from carbon and proton spectra deviate in different directions from a certain specified value, assumed to be true. It is quite obscure what happens in olefins and therefore care must be exercised in the interpretation of these data, except perhaps for compounds (XV) and (XVI).

Another explanation of the discrepancy in the values of $J(^{13}C-H)$ is possible. It is known from the work of Mislow[8,76] that the s-character of a bond can be expressed in terms of the "hybridisation parameter" of the bond λ_i^2, so that

$$\% S = \frac{100}{1+\lambda_i^2}. \qquad (3)$$

λ_i^2 can be readily calculated if the geometry of the molecule is known. Such calculation for ethylene (adopting the σ,π-model) yields λ^2 = 2.2 for the C–H bond and λ^2 = 1.7 for the C=C σ-bond. Hence on combining Eqns. (2) and (3) we obtain $J(^{13}C-H)$ = 156 c/s, which is almost identical with the experimental value. Thus in simple olefins C–H bonds have a somewhat enhanced p-character (in the case of ethylene we have $sp^{2.2}$) compared with the requirement for an sp^2-hybridised atom.

The increase in the s-character of the =C–H bond should be reflected also in the chemical shift of the olefinic proton. The degree of shielding of the proton then decreases and the signals are displaced in the direction of decreasing field. Data on chemical shifts are presented in Table 3. The shift of the signals due to the olefinic protons with increasing cisoid strain has been observed in a fairly large number of examples. Thus τ for olefinic protons is 3.36 for barrelene (XIII)[77], 3.45 for bicyclo[2,2,0]hexadiene (XVIII)[78], 3.47 for the diester (XIX)[79], and 3.27 for the lactone of 3-hydroxycyclobutene-4-carboxylic acid (XX)[80].



(XIX) (XX) (XXI).

2. Infrared Spectra

In the region of =C–H vibrations unsubstituted cyclo-olefins exhibit two frequencies corresponding to symmetrical and asymmetric vibrations[81] (ν^{s}_{C-H} and ν^{as}_{C-H}), which are given in Table 3. The assignment in some studies[62,82] of the frequency 3126 cm^{-1} in the cyclobutene spectrum to ν^{as}_{C-H} is incorrect; this frequency can be readily interpreted as an overtone of the vibrations of the C=C bond[83]. This is also true of norbornene and some of its derivatives[84]. Calculations on the infrared spectrum of cyclobutene showed that the vibration frequency ν^{as}_{C-H} should be 3019 cm^{-1}, i.e. lower than the vibration frequency ν^{s}_{C-H} (3061 cm^{-1})[83].

The ν^{s}_{C-H} vibration frequency of *cis*-but-2-ene, which is 3023 cm^{-1} according to Wiberg and Nist[62] and 3034 cm^{-1} according to Sverdlov and Krainov[85], may be quoted for comparison. An absorption band near 3300 cm^{-1} is characteristic of the ≡C–H bond[81]. It is evident from the data in Table 3 that the ν^{s}_{C-H} vibration frequency increases systematically with decreasing ring size and hence with increasing double bond strain.

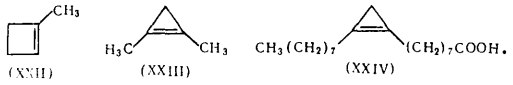
The vibration frequency of the C=C bond in unstrained olefins is near 1650–1660 cm^{-1} (1658 cm^{-1} for *cis*-but-2-ene[62]); data for cyclo-olefins are presented in Table 3, which shows that, as the ring size decreases, this band is initially displaced towards lower frequencies, in cyclopentene and cyclobutene, and then the frequency increases again in the case of cyclopropene. This phenomenon occurs also in the spectra of other compounds. Thus, as already pointed out above, the double bond in cyclononatriene (I) is almost unstrained [according to Eqn. (I), E_{strain} for a single double bond is 0.56 kcal mole^{-1}], which is confirmed by the presence of the frequency 1641 cm^{-1}.[15] However, in triquinacene (XXI)[86], which has a geometry similar to that of compound (I), the strain is higher. This is also shown in the infrared spectrum of compound (XXI), which contains the frequencies 3050 and 1613 cm^{-1}.

Comparison of the C=C stretching vibration frequencies shows that the double bond in norbornene is strained approximately to the same extent as the double bond in cyclobutene. The presence of a frequency in the region 1550–1575 cm^{-1} provides a means of ready identification of the double bond in derivatives of this type[84].

This unexpected decrease of the C=C bond frequency has been explained by a decrease of its force constant[62,82]. However, Sverdlov and Krainov's calculation[83] of the infrared spectrum of cyclobutene showed that the normal value of this force constant can be used. The frequency of the C=C bond depends (for substitution of the same type) on the C=C–C angle. The coefficient of the kinematic interaction of the C=C and C–C bonds is proportional to the cosine of the angle between these bonds. The coefficient is -0.064 for *cis*-but-2-ene, -0.946 for cyclopentene, and -0.009 for cyclobutene; thus the interaction of the coordinates Q(C=C) and Q(C–C) decreases in this series, which results in a decrease of the vibration frequency of the C=C bond. From this point of view, the higher value of this frequency in cyclopropene is reasonable, since the coefficient for the latter compound is 0.054.

It is also interesting to examine the effect of substitution at the double bond on the C=C vibration frequency. In unstrained olefins transition from a *cis*-disubstituted double bond to a trisubstituted double bond causes an increase in frequency from 1650 to 1670–1680 cm^{-1}, i.e. Δ_1 is 20–30 cm^{-1}, and transition to the tetrasubstituted double bond

entails an increase from 1650 to 1680–1690 cm^{-1}, i.e. Δ_2 is 30–40 cm^{-1}. Nevertheless for norbornene derivatives Δ_1 = 60–65 cm^{-1} and Δ_2 = 86–90 cm^{-1},[84] i.e. the frequency increase due to increasing degree of substitution becomes much higher as the strain increases. Similarly, it follows from the infrared spectroscopic data for 1-methylcyclobutene (XXII)[87] that here Δ_1 (relative to cyclobutene) is 70 cm^{-1}.



(XXII) (XXIII) (XXIV).

This relation is shown particularly clearly for cyclopropene derivatives. For 1,3,3-trimethylcyclopropene (XVI)[88] (1768 cm^{-1}), 1,2-dimethylcyclopropene (XXIII)[89] (1898 cm^{-1}), and sterculic acid (XXIV)[90] (1865 cm^{-1}), Δ_1 = 118 cm^{-1} and Δ_2 = 224–257 cm^{-1}.

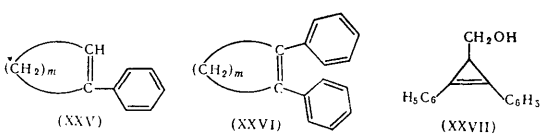
The spectrum of *trans*-cyclo-octene[24] (Table 3) merits special examination. For comparison, the frequencies 3010 and 1650 cm^{-1} in the infrared spectrum of *cis*-oct-4-ene and the frequencies 3027 and 1670 cm^{-1} in the spectrum of *trans*-oct-4-ene may be quoted. Table 3 shows that in the infrared spectrum of *trans*-cyclo-octene the ν^{S}_{C-H} vibration frequency is lower, although this compound is considerably strained. Allinger[24] explained this phenomenon on the grounds of torsional strain in *trans*-cyclo-octene. The presence of a dipole moment (in consequence of torsional strain) explains the appearance of the C=C vibration frequency in the infrared spectrum of *trans*-cyclo-octene, while in the usual symmetrical *trans*-olefins this frequency is forbidden and is observed in Raman spectra.

Thus different relations may obtain in the infrared spectra depending on the different types of strain of the double bond. This can also be illustrated using compounds with unilateral compressive strain of the double bond, the infrared spectroscopic data for which are presented in Table 2. This table also lists the frequencies of the C=O group in the corresponding ketones. It is evident from Table 2 that the frequency of the C=CH_2 bond increases with decreasing ring size, i.e. in conformity with the mode of rehybridisation. The frequency of the carbonyl group in the corresponding ketones varies similarly. For comparison, we may point out that carbon monoxide[91] has an absorption band at 2143 cm^{-1}, while the absorption band of the carbonyl group in keten[92] in the gas phase is 2151 cm^{-1}.

On the other hand, in olefins with unilateral repulsion strain the C=C frequency decreases from 1661 cm^{-1} in 1-ethyl-1-methylethylene to 1644 cm^{-1} in 1-isopropyl-1-methylethylene and 1638 cm^{-1} in 1-t-butyl-1-methylethylene[27], in agreement with the change in hybridisation.

3. Ultraviolet Spectra and Other Properties

There are a few published data on the ultraviolet spectra of certain simple cycloalkenes[62,101] but it is difficult to arrive at any definite conclusions on their basis.

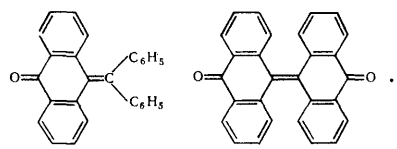


(XXV) (XXVI) (XXVII).

The relations concerning the positions of the absorption bands of derivatives with different functional groups in which the chromophoric group is conjugated with the double bond are also few. Thus Table 3 lists the absorption maxima of the phenyl derivatives of cyclo-olefins of the type of (XXV) and (XXVI). These data show that there is a definite shift of the absorption maximum to the long-wavelength region with increase in the strain of the double bond. There is an indication in the literature of a steady variation in the ultraviolet spectra of unsaturated dicarboxylic acids[102,103], but the available data are incomplete and definite conclusions cannot be arrived at.

Particular interest attaches to an examination of the ultraviolet spectra of olefins with torsional strain of the double bond. As already stated, rotation about the axis passing through the carbon atoms of the double bond causes mutual approach of the energy levels of the ground and excited states. This is evident from Fig. 1, where the potential energy curves for the ground singlet (N) and triplet (T) states and also the excited singlet (V) state for ethylene are plotted schematically; clearly, for those olefins which can give rise to *cis*- and *trans*-isomers, the curves of the type shown in Fig. 1 should be asymmetric.

The ultraviolet absorption band of the usual olefins is due to the $N \rightarrow V$ transition. For an unstrained olefin, this transition is denoted by n_1 in Fig. 1. If the double bond in the ground state is subject to torsional strain and is rotated by an angle φ_1, the ultraviolet absorption maximum in the spectrum of such an olefin is due to the n_2 transition. Hence it is seen that in the presence of torsional strain there should be a bathochromic shift in the ultraviolet spectrum. This has been studied in special detail in the spectrum of dibiphenylene-ethylene (VII)[104]:



(XXVIII) (XXIX).

Eaton and Lin[105] have shown that, on irradiation with ultraviolet light, Δ^2-*cis*-cyclo-octenone isomerises smoothly to Δ^2-*trans*-cyclo-octenone. These workers[106] and also Corey and coworkers[107] obtained in this way the extremely strained *trans*-cycloheptenone, although *trans*-cycloheptene has not so far been isolated[108].

Another very interesting phenomenon, namely thermochromism, is possible for compounds with torsional strain. One of the possible interpretations of this phenomenon was given by Grubb and Kistiakowsky[109], using diphenylmethyleneanthrone (XXVIII), bianthrone (XXIX), and their analogues as examples. A simplified explanation of the phenomenon may be based on Figs. 1 and 2. Torsional strain in

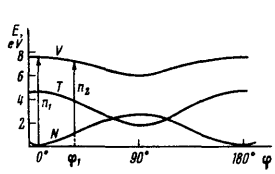


Fig. 1. Potential energy curves as a function of the angle of rotation about the double bond in ethylene; data of Mulliken and Roothaan[29] and Burnell.[30]

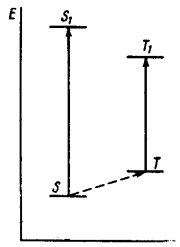


Fig. 2. Schematic representation of the electronic transitions in compounds of the type of (XXVIII), according to the data of Grubb and Kistiakowsky.[109]

systems of the type of (XXVIII) is so much greater than the energy of the ground singlet state that thermal excitation of the molecules to the lower triplet level becomes possible (Figs. 1 and 2). Therefore triplet–triplet transitions can occur in the absorption spectrum of such a compound (Fig. 2). If the excited triplet level is below the excited singlet level, a bathochromic shift occurs. When diphenylmethyleneanthrone (XXVIII) is heated, the colour changes from yellow to red, the colour change being fully reversible as the temperature is varied.

This explanation of thermochromism has been confirmed by quantum-mechanical calculations[110], and also by the study of the temperature variation of paramagnetism. A more rigorous and detailed examination of thermochromism and also other views on this problem have been described by Woodward and Wasserman[111] and Day[112].

Hoijtink[113] showed that the half-wave potential in the polarographic reduction of dibiphenylene-ethylene (VII) is intermediate between the experimental potentials for systems with planar and perpendicular disposition of aromatic rings.

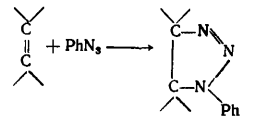
V. CHEMICAL PROPERTIES OF STRAINED OLEFINS

The strain of the double bond is clearly shown not only in physical but also in chemical properties of olefins. These compounds are characterised by high rates of reactions typical of normal olefins. However, reactions characteristic of strained olefins only and also the changes in the stereochemistry of the reactions under the influence of molecular strain are of greatest interest; these will be examined in the present section.

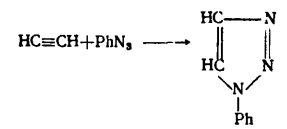
1. Addition Reactions

Addition to the double bond is accompanied by a change in the hybridisation of the carbon atoms — from the sp^2- to the sp^3-hybrid state. The valence angle then decreases from 120° and 109.5°. Therefore, according to the concept of *I*-strain[114], addition should take place readily with compounds having cisoid compressive strain, unilateral compressive strain, and out-of-plane strain. Compounds with torsional strain should also be very reactive, due to the decrease in the degree of overlap of *p*-electrons. The tendency to undergo addition can be inferred from the heat of hydrogenation. Strained olefins react particularly readily by a molecular mechanism involving the formation of cyclic polycentric transition states. 1,3-Dipolar addition and diene synthesis are the most characteristic examples of reactions of this kind.

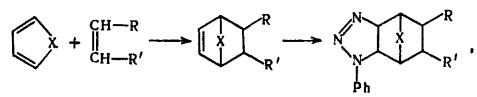
A widely known specific reaction of strained olefins is the reaction with phenyl azide, resulting in the formation of triazolines:



This reaction was investigated in detail by Alder and Stein[115,116] and is widely used nowadays as a kind of "test" for the strained double bond. Unstrained olefins, without electron-acceptor groups, do not undergo this reaction or undergo it with considerable difficulty. According to Dimroth and Fester[117], acetylene reacts with phenyl azide to form phenyltriazole:



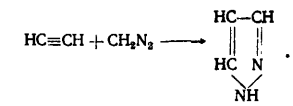
This reaction has been particularly widely used for the identification of diene synthesis adducts of the cyclopentadiene and furan series, since the resulting norbornene and 7-oxabicyclo[2,2,1]heptene contain strained double bonds[118–120]:



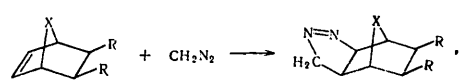
where X = CH_2 and O.

Trans-cyclo-octene reacts extremely vigorously with phenyl azide, while addition to the *cis*-isomer takes place only on standing for several weeks[121]. *Trans*-cyclononene and *trans*-cyclodecene also react with phenyl azide[122–124], while the *cis*-isomers do not react (earlier it was believed erroneously that *trans*-cyclodecene does not give a phenyltriazoline derivative).

Diazomethane does not usually add to the double bond without electron-acceptor substituents[125]. However, Pechmann[126] showed that acetylene readily reacts with diazomethane to form pyrazole:

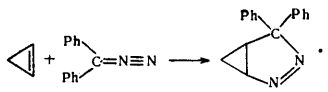


Bearing in mind the analogy between the properties of acetylenes and olefins with cisoid compressive strain, it might have been expected that the latter will also react with diazomethane. Indeed, Zefirov et al. showed that norbornene and also derivatives of 7-oxabicyclo[2,2,1]heptene readily combine with diazomethane to form the corresponding Δ^2-pyrazolines[127,128]:

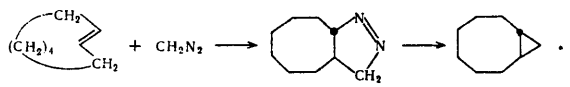


where X = CH_2 and O.

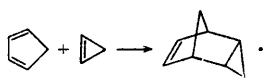
Paul et al.[129] found that cyclobutene also readily combines with diazomethane, but cyclopentene reacts with difficulty, and cyclohexene almost does not react at all (yield 2%). Wiberg and Bartley[130] discovered that cyclopropene readily reacts with diphenyldiazomethane as follows:



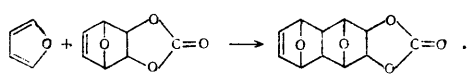
Trans-cyclo-octene also reacts with diazomethane with formation of pyrazoline, which is readily converted into *trans*-bicyclo[6,1,0]nonane under the action of ultraviolet light[131]:



Olefins with cisoid strain of the double bond readily undergo the diene synthesis reaction. For example, cyclopentadiene reacts with cyclopropene at 0°,[130] while the reaction with ethylene requires an elevated temperature and pressure[132]:



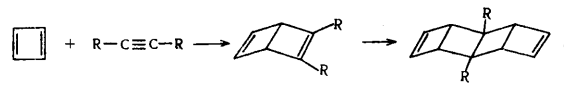
Strained olefins of this type undergo diene synthesis even with relatively unreactive dienes. It has been noted in a number of studies[133,134] that, by virtue of its aromatic nature, furan is an unreactive diene and can react only with very active dienophiles such as maleic anhydride, acetylenedicarboxylic esters, and fumaronitrile. The diene synthesis reaction of furan with dienophiles without electron-acceptor groups takes place under very severe conditions and with a low yield (5% in the case of ethylene[135]) or not at all. However, furan reacts fairly smoothly with bicyclic olefins having a strained double bond[136]:



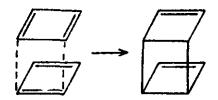
Nowadays diene synthesis with furan is often used for the identification of unstable strained olefins, such as, for example, *trans*-cycloheptene[108], benzocyclobutadiene[137], *trans*-cyclo-octenone[105], and *trans*-cycloheptenone[106]. We may note that compounds of the type of dehydrobenzene are also usually identified by the formation of an adduct with furan[138].

Trans-cyclo-octene also readily undergoes diene synthesis. Ziegler and coworkers[124,139] showed that the reaction of this compound with hexachlorocyclopentadiene takes place easily at 0°, while the *cis*-isomer reacts only on heating to 100°. It is interesting that *cis-trans*-cyclo-octa-1,5-diene readily combines with one mole of hexachlorocyclopentadiene; the second mole adds only on heating.

Strained olefins also readily undergo cyclo-addition reactions. For example, cyclobutadiene reacts with acetylene derivatives to form "Dewar benzene" derivatives[140] and then unusual polycyclobutane derivatives called "pterodactylodienes"[141]:

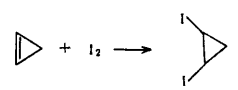


However, in general the reactions of cyclobutadiene can be treated in two ways: as simple cyclo-addition and as a Diels–Alder reaction. The formation of the *syn*-dimer only[140] in the dimerisation of cyclobutadiene is evidence in favour of the second hypothesis (this should be the effect of Alder's rule of "maximum accumulation of double bonds"):

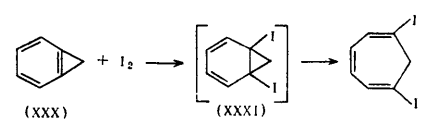


Both possible dimers, *syn*- and *anti*-, were obtained in a pure form by Nenitzescu and coworkers[142,143] by dihalogenation of dichlorocyclobutene.

Iodination of olefins under usual conditions is as a rule reversible; it is well known that the iodide ion is a good 1,2-dehalogenating agent[144]. For this reason, 1,2-di-iodo-derivatives are obtained by photochemical low-temperature iodination of olefins[145]. However, cyclopropene combines with iodine under the usual conditions in carbon tetrachloride solution[130]:



We may note that under these conditions acetylene also combines with one mole of iodine[146]. In 1965 Vogel and coworkers[147] obtained an extremely strained hydrocarbon — benzocyclopropene (XXX) (a substituted system of this type had been obtained earlier[148]), which exhibits reactivity unusual for aromatic compounds. In particular, compound (XXX) combines with iodine in carbon tetrachloride solution, 1,6-di-iodocycloheptatriene being formed together with *o*-iodobenzyl iodide. The authors explain the formation of this compound by the addition of iodine to the "cyclopropene" double bond with formation of the di-iodo-intermediate (XXXI), which then undergoes the Cope rearrangement[149]:



(XXX) (XXXI)

The infrared spectrum of compound (XXX) has an intense band at 1666 cm^{-1}, whose origin is not altogether clear; we may note further that $J(^{13}C-H)$ for the methylene group in compound (XXX) is 178 ± 2 c/s.

The kinetics of reactions involving the addition of diethylaluminium hydride[124] and hexachlorocyclopentadiene[124] to cyclic olefins and also the reduction of the latter by di-isopentylborane[150] and di-imide[151] have now been investigated; these data are presented in Table 4, which shows that, with increasing cisoid strain, the rate of addition increases too. However, an increase of rate has also been observed for cyclo-olefins having rings of moderate

TABLE 4. Relative rates of addition and complex formation reactions for simple cyclo-olefins.

Ring size	Relative rate of addition				Relative complex formation constant	
	of di-imide	of di-iso-pentyl-borane	of hexa-chloro-cyclopenta-diene	of diethyl-aluminium hydride	in water at 25° (Refs. 58 and 153)	in ethylene glycol at 40° (Ref. 66)
C_3					$8.5 \cdot 10^4$ **	
C_4				47		
C_5	15.5	107	22.5	9	6.3	2.0
C_6	1	1	1	1	1	1
C_7	12.1	550 *	30	16	1.2	3.4
C_8 cis	17	2046 *	75	21	0.27	4.0
C_8 trans						280
C_9	5.7		15	6.5		
C_{10}	0.85		0.9	0.8		
Norbornene	450				14.4	17

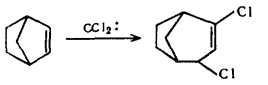
* Data of Garbisch et al.[151]

** Data of Wiberg and Bartley.[130]

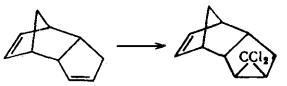
size, with a maximum in the case of cyclo-octene, although these olefins do not have strained double bonds.

Garbisch[152] developed a method of calculation for steric interactions in cyclo-olefins which he applied successfully in an examination of the tautomeric conversions of hydroxymethylene ketones. The application of this type of calculation to reduction with di-imide yielded a satisfactory calculated value of the reaction rate[151]. The success was due to the fact that the polar effects in the reduction with di-imide are very small and the rate of addition is determined by the energy which must be expended in order to change the geometry of the molecule so that a planar transition state arises ("stereotorsional control").

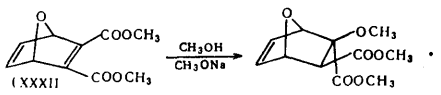
The impression might be created that the increase of molecular strain in all cases results in an acceleration of the rate of addition. However, this is not so. It has been established that norbornene reacts with dichlorocarbene with considerable difficulty[154], a rearrangement product of dichlorocyclopropane being formed:



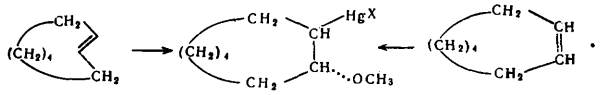
The relative inertness of the norbornene bond is clearly evident in the reaction of dicyclopentadiene from which a monoadduct at the cyclopentene double bond is obtained[155]:



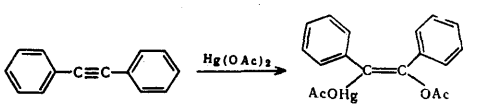
The reason for the retardation of the carbenoid reaction is unknown. We may note, however, that although almost all the "normally" accelerated reactions are of the electrophilic addition type with respect to carbenes, a nucleophilic mechanism cannot be excluded. Nucleophilic addition to a strained double bond has been almost not investigated at all. Thus Zefirov and coworkers[156] showed that nucleophilic addition of methanol to the diester (XXXII) takes place in the normal way without the homoallylic participation of the second double bond:



Finally, the stereochemical aspect of the reactions involving addition to strained olefins must be considered. A number of investigators have shown that the addition of mercury salts to olefins such as norbornene[157-160] or derivatives of 7-oxabicyclo[2,2,1]heptene takes place as *cis*-addition, while hydroxymercuration of unstrained olefins is a *trans*-addition reaction. One of the reasons adduced for the anomalous *cis*-addition is the strain of the double bond in olefins undergoing such addition[160]. Indeed, Sokolov et al.[161] showed that the hydroxymercuration of *trans*-cyclo-octene takes place as *cis*-addition and that of *cis*-cyclo-octene as the normal *trans*-addition:



Burnell[30,162] showed that *trans*-addition reactions at double and triple bonds take place more readily in a twisted conformation. At the same time, such a transition state is difficult to achieve in rigid strained olefins and in the presence of weak electrophilic agents the reaction may take place by a molecular mechanism. In this connection, it is interesting to note that, as shown by Nesmeyanov and coworkers[163,165] and Drefahl[164], the acetoxymercuration of tolane also takes place as *cis*-addition by the mechanism



The reaction with dimethylacetylene does not involve a single pathway[166].

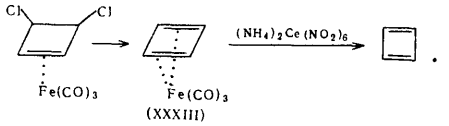
In view of the analogy between the properties of acetylenes and olefins with cisoid compressive strain, in those cases where the stereochemical course of the addition reaction at a double bond is anomalous it would also be useful to investigate the stereochemistry of the addition of the same agent to a triple bond; very little work has been done on this problem.

2. Complex Formation

Lucas and coworkers[167,168] showed that olefins are capable of forming a number of complexes with heavy metal ions and in particular with silver ions. Complexes of this type are formed as a result of the overlapping of the free *s*-orbital of the metal ion and the π-bond of the olefin; the additional stabilisation may be due to the overlapping of the filled *d*-orbitals of the metal and the antibonding π-orbitals of the olefin[6,169,170]. The complexes of silver ions with olefins have been most thoroughly investigated; the instability constants for olefins with unilateral compressive strain are listed in Table 2 and those for olefins with cisoid compressive strain in Table 4. It is evident from Table 4 that in aqueous solutions there is a small but definite increase in the stability of the complexes with increase in the strain of the double bond. Complexes of cyclopropene and also of *trans*-cyclo-olefins are particularly stable. For example, *trans*-cyclo-octene can be extracted from pentane with an aqueous solution of silver nitrate, this being used for its preparative separation from the *cis*-isomer[171]. Data obtained by gas–liquid chromatography on ethylene glycol with added silver nitrate[66] (Table 4) show that the relations which obtain in this case are somewhat different, namely *cis*-cyclo-octene gives a significantly more stable

complex than cyclohexene. The high stability of the complex with norbornene and the extremely high stability of the complex with *trans*-cyclo-octene are striking. There is no correlation between the stability of the complexes of olefins with unilateral compressive strain (Table 2) and the magnitude of the double bond strain itself.

Complex formation is often used for the isolation of unstable olefins. In this connection the history of the attempts made over a period of many years to synthesise cyclobutadiene, which has played an important role in the theory of aromaticity [172], is of interest. Particularly intensive studies have been carried out during the last ten years in the laboratories of Nenitzescu [142,173] and Criegee [174]. The principal idea followed in these studies was stabilisation of cyclobutadiene by formation of a π-complex with a metal. It proved possible to obtain a complex of tetramethylcyclobutadiene with nickel chloride [174]. Only in 1965 was cyclobutadiene synthesised by Pettit's group [140,175], by oxidative decomposition of its iron carbonyl compound (XXXIII), which exhibits the properties of an aromatic system:



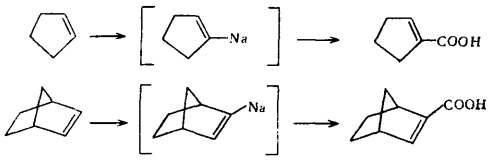
(XXXIII)

According to the calculation performed in 1965 by Dewar and Gleicher [176], cyclobutadiene should have a singlet ground state and its instability should be due to considerable angular strain.

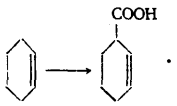
3. Substitution Reactions at the Double Bond

The greater *s*-character of the C–H bond in olefins with cisoid compressive strain results in increased acidity of the hydrogen atoms, similar to that which obtains on going from ethane to ethylene and then to acetylene. The increased acidity of the hydrogen atoms in cyclopropene derivatives has been observed in a number of investigations [88,130]. However, the most convincing data were obtained by Schröder [177] in a study of the base-catalysed deuterium exchange in cyclic olefins. It was found that t-butylacetylene and trimethylcyclopropene readily exchange the hydrogen at the multiple bond even at -20°, the exchange rate constant ratio for these compounds being 1 : 5000. Other cyclo-olefins exchange hydrogen under significantly more severe conditions. Thus bicyclo[3,2,0]heptene slowly exchanges hydrogen even at 110° and rapidly at 139°; cyclopentene exchanges hydrogen at 160°, while *cis*- and *trans*-di-t-butylethylene do not exchange hydrogen at 190°. Norbornene exchanges hydrogen more rapidly than cyclopentene.

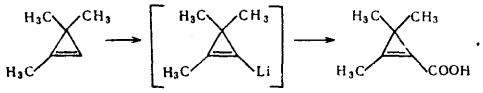
The hydrogen at the double bonds of cyclo-olefins can be substituted by a metal. For example, the action of pentylsodium on norbornene or cyclopentene results in the formation of an organosodium derivative of the cyclo-olefin [178,179], which has been identified by conversion into the corresponding acid:



Cyclohexene yields a $\beta\gamma$-unsaturated acid under these conditions [180]:



Closs and Closs [88] showed similarly that trimethylcyclopropene is readily metallated with butyl-lithium:



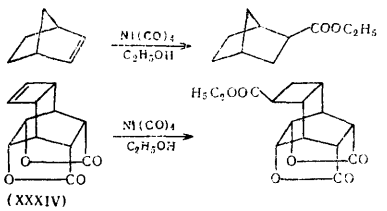
Trimethylcyclopropene reacts with ethylmagnesium bromide similarly as compounds containing a labile hydrogen atom, i.e. with formation of ethane [181]. It is interesting that trimethylcyclopropene forms a fairly stable copper derivative, whose structure, however, has not so far been established [181].

It should be noted that the more pronounced *s*-character of the exocyclic bond in olefins of this type results in a more pronounced electron-acceptor effect in such compounds than in unstrained olefins. Closs and Closs [182] showed that the dissociation constant of trimethylcyclopropenecarboxylic acid is 4.5 times higher than that of *cis*-crotonic acid.

In conclusion we must consider the reaction of unsaturated compounds with nickel carbonyl. Reppe and Kroper [183] showed that this reaction proceeds smoothly with acetylene derivatives having a hydrogen atom at the triple bond, acids being formed:

$$R{-}C{\equiv}CH \xrightarrow{Ni(CO)_4} R{-}CH{=}CH{-}COOH.$$

Ordinary olefins enter into this reaction with difficulty — cyclohexene, for example, yields cyclohexenecarboxylic acid only under very severe conditions. However, Cookson and coworkers [184] showed that norbornene and also the adduct (XXXIV) readily react with nickel carbonyl:



(XXXIV)

The authors explained this course of the reaction by the strain of the double bonds in the reactants.

---oOo---

The above data show that strained olefins exhibit special characteristics both in their physical and chemical properties. Olefins with cisoid compressive strain of the double bond have been most thoroughly investigated. Under favourable conditions it proved possible to calculate the magnitude of the strain in cyclo-olefins and even the rate constants for addition reactions at the double bond. However, many problems have still been little investigated and remain obscure; this applies especially to olefins with other types of strain of the double bond. A detailed quantum-mechanical examination of the problem of strained double

bonds has not been made either. It is still not clear to what extent various types of strained double bonds are chemically equivalent. In this respect olefins with out-of--plane strain are particularly interesting, since, apart from the ease of addition reactions, the rigid structure of certain cyclo-olefins of this type should pre-determine the *cis*-addition of any reagent. There is no doubt that the study of strained cyclo-olefins can lead to the discovery of fundamentally new reactions and also to a deeper understanding of the stereochemical aspects of the known addition reactions.

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EFFECT OF THE SOLVENT ON THE FORMATION AND IONIC DISSOCIATION OF THE ADDUCTS OF ALKALI METALS WITH AROMATIC HYDROCARBONS

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I. INTRODUCTION

The chemistry of the organometallic compounds of the alkali metals is developing fairly rapidly. The adducts of alkali metals with aromatic hydrocarbons have attracted much attention because of their unusual structure [1,2] and because they have found wide application in polymer chemistry [3-7] and in synthetic organic chemistry [5,8,9]. The reactions involving the addition of alkali metals to aromatic hydrocarbons were first investigated by Schlenk [10,11], who established, in particular, that in ethyl ether sodium readily adds to anthracene and phenanthrene but not to naphthalene and biphenyl. However, Scott observed [12] that these hydrocarbons react rapidly and quantitatively with sodium when the solvent is 1,2-dimethoxyethane. Subsequently the adducts of benzene and its homologues with alkali metals were obtained in this solvent [13,14].

Scott [12] noted an appreciable electrical conductivity of the solutions of the adducts, indicating their ionic nature. Hückel and Bretschneider [15], who studied the reactions of alkali and alkaline earth metals with aromatic hydrocarbons in liquid ammonia, suggested that the hydrocarbon is converted into an anion by capturing electrons from the metal atom. Weissman and coworkers [16] showed that solutions of aromatic organosodium compounds in tetrahydrofuran exhibit strong paramagnetic absorption and concluded that the aromatic anion is at the same time a paramagnetic species; it has therefore been called a radical-anion ($Ar^{\cdot-}$). The reaction of an aromatic hydrocarbon (Ar) with an alkali metal can be represented by the equation

$$Ar + M \rightleftarrows Ar^{\cdot-}M^{+}. \quad (1)$$

Laitinen and Wawzonek [17] and Hoijtink et al. [18] obtained radical-ions in the electrolytic reduction of hydrocarbons (see also the reviews of de Boer [2] and Hoijtink [19]). The reaction with polycyclic hydrocarbons proceeds further - a second electron adds to the radical-anion and a doubly charged anion (dianion) is formed.

Measurements of the magnetic susceptibility of the solutions of the adducts of anthracene and phenanthrene with sodium [20] showed that, on more prolonged contact between the solution and the metal surface, the paramagnetic compound formed initially ($Ar^{\cdot-}M^{+}$) is converted into a diamagnetic product as a result of the reaction

$$Ar^{\cdot-}M^{+} + M \rightleftarrows Ar^{2-}2M^{+}. \quad (2)$$

Addition of the hydrocarbon to a solution of its dianions results in the appearance of paramagnetism due to the reaction

$$Ar^{2-}2M^{+} + Ar \rightleftarrows 2Ar^{\cdot-}M^{+}. \quad (3)$$

This is an equilibrium reaction and therefore the dianion can be formed not only by the reduction of the radical-anion, but also by the disproportionation of two radical-anions. Recently the possible addition of three electrons to the decacycline molecule has been observed [21].

The properties of radical-anions have been extensively studied by electron spin resonance and electron spectroscopic methods. The ESR spectra were studied by Weissman and coworkers [22-26] and other investigators [27-29]. The

principal studies on the electronic absorption spectra were carried out by Hoijtink and his school[30,31] (see also Refs. 1 and 2). The interpretation of the spectra within the framework of the molecular orbital method[32-36] leads to the conclusion that the electron in the radical-anion occupies the lowest antibonding orbital of the aromatic molecule. The bond with the metal ion is achieved by the coulombic interaction of the entire π-electron system of the radical-anion. The electronic structure of the adducts of alkali metals with aromatic hydrocarbons has been recently discussed in detail in de Boer's review[2].

The problem of the effect of the solvent and metal on the equilibria in the formation and dissociation of adducts has not so far been elucidated adequately, despite its great importance, in particular for the understanding of anionic polymerisation and other organic anionic reactions. This led us to write the present review on the above problem.

II. SOLVATION OF CATIONS IN ADDUCT FORMATION REACTIONS

The positions of equilibria (1)–(3) involving a particular hydrocarbon depend greatly not only on the nature of the metal but also on the solvent, the latter showing different effects on different metals. This was shown qualitatively by Schlenk[10,11] and Scott[12]. Thus, in contrast to lithium, sodium does not react with naphthalene and biphenyl in ethyl ether, but in methyl ether adducts are formed. Potassium interacts with naphthalene and biphenyl even in octane and toluene[37]. The equilibrium concentrations of the radical-anions of benzene[38] formed in the reaction with lithium and potassium in 1,2-diethoxyethane, are higher by approximately two powers of ten than in the reaction with sodium, and the relative concentrations of toluene radical-anions[38] are 100 in 1,2-dimethoxyethane, 30 in 1-ethoxy-2-methoxyethane, and 3 in 1,2-diethoxyethane. Pudovik and Muratova[39] showed that a red dilithium derivative of naphthalene (the solution of naphthalene radical-anions is green) forms in dimethoxymethane and in dioxan. According to Garst's data[40], the nature of the solvent and the metal is important in radical-anion disproportionation reactions.

The pronounced dependence of equilibrium (1) on the nature of the metal and solvent can be explained by an examination of the energy balance in the formation of radical-anions[4]:

$$\Delta H = L + I - E_{Ar} - S_{M^+} - S_{Ar^-} - Q, \qquad (4)$$

where ΔH is the enthalpy of the reaction, L the heat of sublimation of the metal, I its ionisation potential, E_{Ar} the electron affinity of the aromatic hydrocarbon, S_{M^+} and S_{Ar^-} are the heats of solvation of the metal cation and the radical-anion, and Q is the energy of the coulombic interaction of the ions. The electron affinity of the aromatic hydrocarbons (in electron-volts) increases in the sequence[41] benzene (-0.54), biphenyl (0.41), naphthalene (0.65), phenanthrene (0.69), anthracene (1.19). The heats of sublimation and the ionisation potentials of alkali metals and the radii (r) of their cations are presented in Table 1.

The larger is the sum $L + I$ the less vigorous should be the reaction of the metal. In fact, Table 2 shows that the yields of biphenyl radical-anions do not vary with the metal in the same way in different solvents[42]. This is due to the large contribution to the energy of reaction (1) by the heat of solvation of the cations, which is markedly influenced by the solvent.

TABLE 1. Constants of alkali metals[43].

Metal	L, kcal mole^{-1}	I, eV	r, Å
Li	32.2	5.39	0.78
Na	23.4	5.14	0.98
K	18.9	4.34	1.33
Rb	18.0	4.18	1.49
Cs	16.3	3.89	1.65

TABLE 2. Relative concentrations of biphenyl adducts.

Solvent	Li	Na	K
1,3-Dimethoxypropane	100	7	30
1,2-Diethoxyethane	45	15	65
Tetrahydrofuran	100	45	30
Tetrahydropyran	80	10	6

Approximate calculation shows[44] that the heats of solvation do indeed constitute an appreciable fraction of the heat of reaction (1), as a result of which the formation of the hydrocarbon radical-anion in electron-donor solvents is in most cases exothermic. Solodovnikov[29] estimated the heat of reaction of benzene with potassium in 1,2-dimethoxyethane from the temperature variation of the intensity of the ESR signal due to the benzene radical-anion. In the temperature range 233–273°K the heat of reaction is about 20 kcal mole^{-1}.

The temperature variation of the equilibrium constant (K) for the reaction of sodium with biphenyl in certain ethers and their mixtures with n-heptane has been investigated spectrophotometrically[42,45,46]. The enthalpies (ΔH) and entropies (ΔS) of reaction were calculated from the results by the method of least squares using the equation $\ln K = -\Delta H/RT + \Delta S/R$. The values of K_{273}, ΔH, and ΔS and also the temperature range in which these parameters were determined are listed in Table 3. The equilibrium constants were determined without taking into account the activity coefficients. However, this does not prevent a comparison of the effects of solvents (with similar dielectric constants and dipole moments — see Table 5) on the thermodynamics of the formation of the adduct.

The data in Table 3 show (cf. Nos. 1 and 19) that the variation of ΔH when the reaction is carried out in different solvents is as much as ~ 25 kcal mole^{-1}. This confirms what has been said above about the importance of the contribution of the heat of solvation to the energy of the reaction. The absolute values of ΔH, obtained under comparable conditions, decrease in the series dimethyl ether of diethylene glycol > 1,2-dimethoxyethane > 1-ethoxy-2-methoxyethane > 1,2-dimethoxypropane > tetrahydrofuran > 1,2-diethoxyethane > 1,3-dimethoxypropane > tetrahydropyran.

As a result of the ordering of solvent molecules in the solvation shells of the ions, the entropy of the system decreases and the entropy of reaction ΔS is negative. The degree of ordering is higher the more stable is the solvate and therefore on changing the solvent the absolute values of ΔH and ΔS vary in unison, the effects of their variation on the free energy of reaction ($\Delta F = \Delta H - T\Delta S$) cancelling out, so that the variation of the latter is 1–2 kcal mole^{-1}.

TABLE 3. Thermodynamic parameters for the formation of sodiobiphenyl in various solvents [45,46].

No.	Solvent	K_{273}	T, °K	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
1	dimethyl ether of diethylene glycol–heptane*	—	318—298	31	100
2	1,2-dimethoxyethane–heptane**	—	318—303	13.0±0.5	43±2
3	ditto	—	303—283	18.0±0.6	61±2
4	1-ethoxy-2-methoxyethane	7.2	318—273	17.4±0.5	60±2
5	1-ethoxy-2-methoxyethane–heptane**	—	303—283	12.2±0.2	46±2
6	ditto	2.1	283—268	20.0±0.8	71±3
7	1-ethoxy-2-methoxyethane–ethyl ether**	—	303—283	14	50
8	ditto	4.8	283—273	25	87
9	1,2-diethoxyethane	0.2	293—258	9.6±0.4	39±2
10	ditto	—	258—243	22.0±1	86±4
11	1,2-diethoxyethane–heptane**	0.1	283—258	7	30
12	ditto	—	258—243	16	64
13	1,2-dimethoxypropane	4.6	318—273	16.5±0.7	58±3
14	1,3-dimethoxypropane	0.04	263—238	15.5±0.3	63±1
15	tetrahydrofuran	1.4	313—263	11.2±0.5	40±2
16	tetrahydrofuran–heptane***	—	303—283	5.5	21
17	ditto	0.7	283—263	8.5	31
18	»	—	263—253	14	54
19	tetrahydropyran	0.06	273—228	6.8±0.2	31±1

* The volume ratio of the ether and heptane in the mixture was 1:1.4.

** 4.3:1.

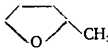
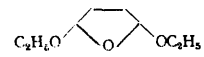
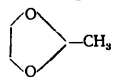
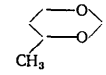
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Thermodynamic data have also been obtained spectrophotometrically for the reaction of sodium with naphthalene in 1,2-diethoxyethane [45] and for the reaction of sodium with 4-ethylbiphenyl and *N*-ethylcarbazole in tetrahydrofuran [47].

The above thermodynamic data give an idea of the relative solvating power of a number of ethers. More detailed information about its variation with the structure of the solvent molecules can be obtained from Table 4, which gives the relative equilibrium concentrations of sodiobiphenyl (C_{sb}) and sodionaphthalene (C_{sn}) formed at room temperature in the presence of a sodium mirror of large area at the same concentrations of hydrocarbon solutions (arbitrarily defined as 100) in 31 ethers and acetals [42,48]. The values of C_{sb} were determined at the same time by electron spin resonance, the results agreeing satisfactorily with the spectrophotometric measurements (the values of C_{sb} in Table 4 are averages of the results of both methods). If biphenyl was quantitatively converted into the adduct in ethereal solution, i.e. C_{sb} = 100, the ether was diluted with n-heptane and the value of C_{sb} in Table 4 refers to an equimolar mixture of the ether and n-heptane. The last column of Table 4 lists the shifts ($\Delta\nu_{OD}$) of the stretching vibration frequency of the OD bond in the infrared spectrum of deuteriomethanol CH_3OD on formation of the hydrogen bond with the oxygen atom of the ether [49]. According to Gordy [50], $\Delta\nu_{OD}$ is a measure of the electron-donor properties (basicity) of the ethers.

The results in Table 4 may be compared with independent data on the effects of solvents on the spectra of the adducts or the electrical conductivity of their solutions, which according to a number of workers [51-54] also reflect the effect of the solvation of the alkali metal cation. According to these studies, the variation of the solvating power of the ethers (1,2-dimethoxyethane > tetrahydrofuran > tetrahydropyran, methyltetrahydrofuran > 1,4-dioxan) is the same as the sequence corresponding to the decrease of C_{sb} and C_{sn} in these solvents (Nos. 4, 23–26 in Table 4).

TABLE 4. Effect of the structure of solvent molecules on the equilibrium concentrations of the adducts of sodium with biphenyl (sb) and naphthalene (sn) and on the electron-donor properties of the ethers [48,49].

No.	Solvent	C_{sb}	C_{sn}	$\Delta\nu_{OD}$, cm^{-1}
	a. Effect of the size of the alkyl groups in ethers with one and two oxygen atoms			
1	CH_3OCH_3	2	20	—
2	$CH_3OC_2H_5$	1	3	—
3	$C_2H_5OC_2H_5$	1	2	106
4	$CH_3OC_2H_4OCH_3$	100	100	93
5	$CH_3OC_2H_4OC_2H_5$	60	100	95
6	$CH_3OC_2H_4OC_3H_7$	22	85	97
7	$CH_3OC_2H_4OC_4H_9$	20	82	95
8	$CH_3OC_2H_4OC_5H_{11}$	15	70	98
9	$C_2H_5OC_2H_4OC_2H_5$	15	60	98
10	$C_4H_9OC_2H_4OC_4H_9$	10	20	100
	b. Effect of the structure of the bridge between the oxygen atoms in glycol ethers			
11	$CH_3OCH_2OCH_3$	0	0	84
	$CH_3O(CH_2)_2OCH_3$	100	100	93
12	$CH_3O(CH_2)_3OCH_3$	7	50	100
13	$CH_3O(CH_2)_4OCH_3$	3	20	104
14	$CH_3O(CH_2)_5OCH_3$	—	6	104
	$C_2H_5O(CH_2)_3OC_2H_5$	15	60	98
15	$C_2H_5O(CH_2)_3OC_2H_5$	—	14	106
16	$C_2H_5O(CH_2)_4OC_2H_5$	—	10	106
17	$CH_3OCH(CH_3)OCH_3$	0	7	91
18	$CH_4OCH(CH_3)CH_2OCH_3$	45	90	96
19	$CH_3OCH(CH_3)CH(CH_3)OCH_3$	17	85	100
	c. Effect of the number of units and the type of alkyl substituents in poly(ethylene glycol) ethers (data for the reaction of sodium with biphenyl in mixtures of ethers with heptane)			
20	$CH_3O(C_2H_4O)_3CH_3$	100	—	90
21	$CH_3O(C_2H_4O)_2CH_3$	100	—	90
	$CH_3OC_2H_4OCH_3$	15	—	93
22	$C_2H_5O(C_2H_4O)_2C_2H_5$	35	—	98
	d. Effect of the size of the ring, the number of oxygen atoms, and the type of substituents in cyclic ethers			
23		45	85	115
24		10	50	112
25		4	35	100
26		10	55	114
27		0	5	92
	e. Effect of the size of the ring and the position of the substituents in cyclic acetals			
28		10	70	76
29		15	70	85
30		—	15	88
31		—	30	85

From this point of view, comparison of the results of Shatenshtein et al. [48] and those of Garst et al. [55] is of greatest interest. The latter worker observed that the position of the principal band in the absorption spectrum of the ketyl of sodiobenzophenone depends on the solvent. From the standpoint of the postulate of the ionic nature of ketyls [56,57],

the author explained the shifts of the absorption band by the variation of the interionic interaction due to the differences in the degree of solvation of the Na^+ cation in different solvents. According to McClelland's theoretical findings[57], the band is displaced more towards the red region of the spectrum the higher is the solvating power of the solvent. Then it follows from the data of Garst et al.[55] that the degree of solvation of the Na^+ cation decreases in parallel with C_{sb} and C_{sn} in the same solvents (Table 5).

The phenomenon of cation solvation cannot be explained if solvation is regarded as a purely electrostatic ion–dipole interaction. This is shown by the data in Table 3 on the thermodynamics of the formation of biphenyl radical-anions in different solvents taking into account their polar properties, by the absence of correlation between other parameters reflecting the differences in the solvating power of the solvents and their dielectric constants and dipole moments (see Table 5).

The results can be readily interpreted if the solvation is regarded as complex formation, i.e. a process of the donor–acceptor type. This approach enabled Izmailov[63] to explain the characteristic features of the hydration of alkali metal cations. The electron donors are oxygen atoms which have unshared electron pairs and the cation is the acceptor which provides vacant electron orbitals. The number and direction of the donor–acceptor bonds are determined by the multiplicity and type of hybridisation of the free orbitals of the cations. The probable vacant orbitals in Li^+, Na^+, and K^+ are $2s2p$, $3s3p$, and $4s4p3d$, the type of hybridisation of which is sp^3, sp^3, and sp^3d^2 respectively according to Eyring et al.[64] Thus in the solvation of Na^+ the oxygen atoms of the ligand must be located at the vertices of a tetrahedron with the cation at its centre. The greatest contribution to the heat of solvation comes from the energy of formation of the donor–acceptor bond between the cation and the solvent molecules. The secondary solvation of the cations takes place by ion–dipole interaction, whose energy makes a smaller contribution to the total solvation energy.

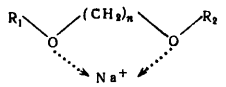
The above considerations hold also in the solvation of alkali metal cations by ethers. The more pronounced are the electron-donor properties of the oxygen atom of the given ether, the higher is the solvation energy and at the same time the stronger is the hydrogen bond formed between the ether molecules and CH_3OD. Therefore one should expect a correspondence between the relative concentrations C_{sb} and C_{sn} and $\Delta\nu_{OD}$ in the ether series. However, according to the data in Table 4 there is no such correlation. For example, the electron-donor properties of ethylene glycol ethers increase on substituting one or both CH_3 groups in 1,2-dimethoxyethane by alkyl groups with a larger number of carbon atoms, as a result of the higher inductive effect ($+I$) of such substituents, but the solvation of the Na^+ ion is then weakened. The inductive effect of the oxygen atom is of the opposite sign ($-I$) and therefore, as the methylene bridge separating the oxygen atoms in glycol ethers becomes longer, the latter become stronger bases, and yet the most stable solvate is formed by 1,2-dimethoxyethane. These discrepancies can be explained by the fact that steric factors, which play an important role in the solvation of the cation, have virtually no effect on the formation of the hydrogen bond.

TABLE 5. Comparison of the relative concentrations C_{sb} and C_{sn} with the position of the principal band (λ_{max}, nm) in the spectrum of sodiobenzophenone and the dielectric constants (DC) and dipole moments (μ) of the solvents*.

Solvent	C_{sb}	C_{sn}	λ_{max}	DC$_{25}$°	μ
Dimethyl ether of diethylene glycol	—	—	704	7.25[58]	—
1,2-Dimethoxyethane	100	100	697	6.96[58]	1.72[61]
1-Ethoxy-2-methoxyethane	60	100	—	5.77[58]	1.68[61]
Tetrahydrofuran	45	85	675	7.31[58]	1.87[62]
2-Methyltetrahydrofuran	10	50	654	4.6[59]	—
1,2-Diethoxyethane	15	60	—	4.89[58]	1.65[61]
Tetrahydropyran	10	50	—	5.4[59]	1.87[62]
1,4-Dioxan	4	35	643	2.23[59]	0.4[62]
Dimethylacetal	0	7	642	—	—
Ethyl ether	0	2	632	4.22[59]	1.22[62]
Dimethoxymethane	0	0	628	2.65[60]	0.67[62]

* The superscript numbers indicate the references to work from which the values of the dielectric constants and dipole moments have been taken.

The nature of the steric hindrance may be deduced using the glycol ethers as an example. Studies of the formation of complexes of titanium tetrafluoride[65] or tin tetrachloride[58] with ethers containing two oxygen atoms show that the latter are capable of forming two bonds with an acceptor. The dipole moment of the complex $SnCl_4.2C_2H_5OC_2H_4OC_2H_5$ corresponds to the octahedral model with *cis*-disposition of the oxygen atoms. It may be supposed that the reaction of the ethylene glycol ether with Na^+ ions involves the formation of a chelate complex:



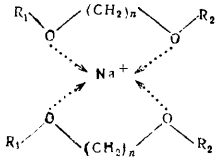
The postulate of the chelate complexes of alkali metals was put forward by Sidgwick[66] as early as the 1920's. Since then it has often been used[59,67–69] to account for the high solvating power of 1,2-dimethoxyethane in various anionic organic reactions.

The structure of the methylene bridge is of great importance for the formation of a stable solvate. The atomic grouping characteristic of ethylene glycol ethers $[-O(CH_2)_2O-]$ must be regarded as the most favourable. For example, even in 1,2-dibutoxyethane the values of C_{sb} and C_{sn} are higher than in 1,3-dimethoxypropane and other dimethyl ethers of higher glycols. This feature of the steric hindrance is associated with the stability of the *cis*-conformation of the molecule, which is necessary for the formation of the chelate. As the number of CH_2 groups freely rotating relative to one another increases, the transition of the molecule to this conformation becomes increasingly difficult. The occurrence of free rotation about all the C–C and C–O bonds in glycol ether molecules was confirmed[61] by the agreement of the experimental dipole moments with those calculated theoretically on the basis of this hypothesis. Free rotation accounts also for the decrease of the solvating power of ethylene glycol ethers with increase in the size of alkyl side-groups, since the possibility of the screening of oxygen atoms by the latter then increases. We have seen (Table 3) that steric hindrance in the solvation of the metal ion is clearly reflected in the values of the thermodynamic parameters for the formation of the adduct.

It is interesting to note that the stability of the complexes of stannic chloride with glycol ethers[58] as well as the values of C_{sb} or C_{sn} (Table 4) decrease in the following sequence when the number n of methylene groups is reduced: $2 > 3 > 4 > 1$. At the same time the change in the

length of the alkyl groups of glycol ethers affects the formation of complexes with stannic chloride less than the solvation of Na^+ ions, since the stability of the stannic chloride complexes with 1,2-diethoxyethane and 1,2-dibutoxyethane is almost the same. This is not surprising, since usually the more intense is the interaction the smaller is its sensitivity to structural factors.

The data on the thermodynamics of the reaction of sodium with biphenyl also made it possible[45,46] to arrive at certain conclusions concerning the mechanism of the solvation. Thus if the solvent is an ethylene glycol ether or its mixture with heptane, the relation between $\log K$ and $1/T$ is represented by two straight lines of different slopes, and ΔH and ΔS each have two different values, depending on the temperature range in which the reaction has been carried out in the given solvent (Table 3, Nos. 2, 3, 5–12, Fig. 1). This can be explained by a stepwise mechanism of the solvation of the sodium ion. Since its coordination number is four[63] and ethylene glycol ether molecules are capable of forming simultaneously two donor–acceptor bonds each, there are two types of chelate complex — with one (see above) and two ether molecules:



Decrease of temperature favours the formation of coordination-saturated solvates. The absolute values of ΔH and ΔS then increase. Szwarc[70] also concluded that two 1,2-dimethoxyethane or four tetrahydrofuran molecules are involved in the solvation of the sodium ion. The temperature corresponding to the break in the $\log K - 1/T$ linear plots must be regarded as the temperature corresponding to the conversion of one type of solvate into another. It falls with increasing steric hindrance in the solvation: 1,2-dimethoxyethane (303°K) > 1-ethoxy-2-methoxyethane (283°K) > 1,2-diethoxyethane (258°K). The above temperatures were determined for a mixture of ether with heptane[46].

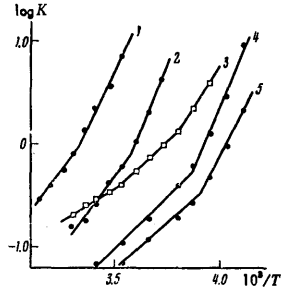


Fig. 1. Variation of $\log K$ for the formation of sodiobiphenyl with $1/T$; solvent: 1) 1,2-dimethoxyethane–heptane; 2) 1-ethoxy-2-methoxyethane–heptane; 3) tetrahydrofuran–heptane; 4) 1,2-diethoxyethane; 5) 1,2-diethoxyethane–heptane.

In contrast to glycol ethers, each tetrahydrofuran molecule can form only one donor–acceptor bond with the cation. It proved possible to demonstrate three solvation steps, of the possible four, on the basis of the temperature variation of the logarithm of the equilibrium constant for the reaction of sodium with biphenyl in a mixture of tetrahydrofuran with heptane (Table 3, Nos. 16–18, Fig. 1). The breaks in the straight line occur at 283°K and 263°K. Judging from the literature data[52] obtained by different methods, the Na^+ cation is fully solvated in tetrahydrofuran only at 200°K. The formation of the coordination-saturated complex (solvate) of the cation is accompanied by a weakening of the coulombic interaction between the ions. Therefore the increment of ΔH for the reaction when the temperature is reduced does not correspond to an additional heat of solvation but to the difference between the latter and the decrease of the coulombic interaction energy.

The hypothesis of the stepwise mechanism of solvation in tetrahydrofuran was put forward by Medvedev, Gantmakher, and coworkers[71] to explain the effect of added ethers on the frequency shift in the spectrum of diphenylalkyl-lithium. It was assumed that two stages in the solvation of the cation in the ion pair are possible — with one and two molecules[72]. The stepwise character of the solvation of lithium alkyls with ether containing one and two oxygen atoms is also reflected in the kinetics of the reaction of butyl-lithium with butyl bromide[73]. The solvation of organic anions by ethers as a result of donor–acceptor interaction is unlikely; the interaction between the solvent and the radical-anion is more probably of a coulombic type. The energy of the solvation of the radical-anion should then be approximately of the same order of magnitude as the energy of the secondary solvation of the cation. Consequently the effect of the solvent on the formation of radical-anions is determined mainly by the solvation of the cation, particularly if account is taken of the fact that differences in the polarity of ethers are only slight.

III. THE ROLE OF CATION SOLVATION IN ADDUCT IONIC DISSOCIATION EQUILIBRIA

The study of the ionic dissociation of adducts in ethereal solutions makes it possible to confirm and extend the above postulates concerning the solvation of cations. Table 6 lists the molar conductances of sodionaphthalene (I — 0.0023 M; II — 0.004 M) multiplied by the viscosity of the solvent[42,45]. Evidently $\Lambda\eta$ decreases by a factor of almost 600 on going from the dimethyl ether of diethylene glycol to tetrahydropyran, although the dielectric constants of the solvents differ little. The sequence of the values of $\Lambda\eta$

TABLE 6. Products of the viscosity and molar conductance of sodionaphthalene solutions at 293°K ($\Lambda\eta$, $cm^2\ \Omega^{-1}\ cP$).[45]

Solvent	$\Lambda\eta$ I	$\Lambda\eta$ II	DC$_{20°}$
Dimethyl ether of diethylene glycol	6.2	5.8	7.25
1,2-Dimethoxyethane	3.3	3.3	6.96
1-Ethoxy-2-methoxyethane	0.77	0.4	5.77
Tetrahydrofuran	0.59	0.44	7.31
1,2-Diethoxyethane	0.09	0.03	4.89
Tetrahydropyran	—	0.01	5.4

corresponds to the solvating power of the solvents (cf. Table 5), since a decrease of the degree of solvation favours ion association. The latter is in general pronounced in ethereal solutions and the adduct is largely present in the form of ion pairs. This follows from the determination of the approximate values of the dissociation constants K_d for the lithium, sodium, and potassium derivatives of naphthalene, calculated[42] by the method of Fuoss and Kraus[74] from measurements of the concentration dependence of the molar conductances (Table 7).

The dissociation constants of the adducts and certain other organometallic derivatives of alkali metals determined by other workers[52,75-79] in tetrahydrofuran solution are also of the order of 10^{-6}–10^{-7} M (Table 8).

The degree of dissociation of lithionaphthalene in 1,2-dimethoxyethane and tetrahydrofuran and also of sodionaphthalene in 1,2-dimethoxyethane at 293°K and a concentration of the order of 0.002 M is approximately 0.1. Under these conditions the value of $\Lambda\eta$ for sodionaphthalene solutions in the dimethyl ether of ethylene glycol is larger only by a factor of two than in 1,2-dimethoxyethane (Table 6), i.e. even in a solvent with a higher solvating power than 1,2-dimethoxyethane the concentration of ion pairs is still high. Dilution of the solution of sodionaphthalene in 1,2-dimethoxyethane to 10^{-4} M increases somewhat the degree of dissociation — approximately to 0.3.

These findings contradict Hoijtink's assertion[51] that sodionaphthalene is completely dissociated in 1,2-dimethoxyethane into free solvated ions. Hoijtink's view was shared by Weissman[52] and a number of other workers[53,54], who investigated the ESR of the radical-anions.

In the ESR spectrum of the sodionaphthalene solution in tetrahydrofuran there is additional splitting, which is absent from the spectrum of the 1,2-dimethoxyethane solution[52]. The intensity of the splitting decreases as the temperature is reduced. At 200°K it almost completely vanishes and the spectrum becomes identical with that of the solution in 1,2-dimethoxyethane. Similar observations were made for solutions of sodionaphthalene in methyltetrahydrofuran, tetrahydropyran, and dioxan[52].

The additional splitting in the ESR spectrum is due to the interaction of the unpaired electron of the radical-anion with the nucleus of the Na^+ cation. Such interaction cannot take place when the ions are free. Therefore Atherton and Weissman[52] suggested that in 1,2-dimethoxyethane the adduct is completely dissociated, while in other ethers it is present mainly in the form of ion pairs. The absence of the additional splitting from the spectrum of the tetrahydrofuran solution at 200°K and below this implies, in view of these investigations, that sodionaphthalene is also completely dissociated under these conditions. The increase of the degree of dissociation as the temperature is reduced can be explained[51] by the increase of the dielectric constant of the solvent. Rowlands and coworkers[81] also observed an additional splitting in the ESR spectra of the radical-anions

TABLE 7. Dissociation constants ($10^6 K_d$, mole litre^{-1}) of naphthalene adducts at 293°K.

Solvent	Li	Na	K
1,2-Dimethoxyethane	16	25	6.5
Tetrahydrofuran	18	1	0.5

TABLE 8. Dissociation constants of adducts in tetrahydrofuran.

Adduct	T,°K	$10^6 K_d$, mole × litre^{-1}	References	Adduct	T,°K	$10^6 K_d$, mole × litre^{-1}	References
Lithionapthalene	293	1.0	75	Sodioterphenyl	298	3.8	76
Sodionaphthalene	295	1.7	52	Sodiopyrene	298	7.0	76
»	293	1.0*	80	Sodioperylene	298	23	76
»	298	0.2*	76	Sodiotetraphenylethylene	298	2.0	77
Sodiobiphenyl	298	1.2	76	Fluorenylsodium	298	0.7	78
Sodioanthracene	298	4.6	76	»	203	40	78
Sodiotetracene	298	15	76	Sodiostyrene	298	0.15	79

* The discrepancy between the values of K_d in Refs. 76 and 80 is due to the different methods of calculation used, the results of the measurements being almost identical. In our view, there is no point in resorting to the more accurate method of calculation, as in Ref. 76, since Λ_∞ is evaluated by extrapolation over a long section of the experimental $\Lambda C - \sqrt{C}$ curve.

of pyrazine and pyridazine (obtained by reaction with sodium) in tetrahydrofuran solution, but not in 1,2-dimethoxyethane. Like Atherton and Weissman[52], they failed to observe the interaction of the unpaired electron with the nucleus of the potassium ion. According to Hush and Rowlands[36], this is due to the insufficient resolving power of the instruments, since examination of the spectroscopic data with the aid of the molecular orbital method leads to the conclusion that in tetrahydrofuran there is powerful ion association of the adducts of naphthalene and anthracene with lithium, sodium, and potassium. Later studies confirmed the validity of this view to some extent. In particular, splitting was observed in the ESR spectra of potassiobiphenyl[82] in tetrahydropyran, dihydropyran, and tetrahydrofuran (quoted in the order of decreasing degree of association) solutions, while the solution in 1,2-dimethoxyethane gave rise to the spectrum of the "free" radical-anion.

Data on the effect of the solvent and the cation on the ion association were obtained also by other investigators using the ESR method. Fraenkel and coworkers[54] showed that the degree of association of cyclo-octatetraene radical-anions with a cation decreases in the following order (the cation and the solvent are indicated): Na^+, tetrahydrofuran > Na^+, dimethoxyethane ≥ Li^+, tetrahydrofuran > Li^+, dimethoxyethane. On the basis of similar experiments, de Boer and Mackor[53] concluded that lithio-, sodio- and potassio-pyracene are completely dissociated into ions in 1,2-dimethoxyethane and completely associated in methyltetrahydrofuran at temperatures in the range between 300° and 180°K. The spectrum of the "free" radical-anion in tetrahydrofuran solution appeared at 183°K in the presence of K^+ and at 193°K in the presence of Na^+, while in the presence of Li^+ it was observed at all the temperatures. Evidently these results[52-54,81,82] are fully consistent with the postulates concerning the relative solvating power of the solvents and the variation of the degree of solvation with the radius of the cation. The contradiction between the conclusion that total dissociation of adducts in ethereal solutions is possible, which was arrived at on the basis of ESR spectroscopic studies, and the results obtained by conductimetric measurements[42,46] can be resolved by means of the hypothesis that two types of ion pairs exist — in contact (I) and separated (II)[46,76,80]. In the latter type the ions are separated by a layer of solvent molecules (Sl)[83,84]. Equilibrium in the dissociation of ion pairs into free solvated ions can be represented by

$$\underset{\text{(I)}}{Ar^-M^+} \overset{\Delta H_1}{\underset{Sl}{\rightleftharpoons}} \underset{\text{(II)}}{Ar^-|Sl|M^+} \overset{\Delta H_2}{\underset{Sl}{\rightleftharpoons}} \underset{\text{(III)}}{Ar^-_{Sl} + M^+_{Sl}} \qquad (5)$$

The position of the equilibrium depends on the type of the adduct, the solvent, and the concentration of the solution and temperature†.

Geske and Maki[86] and McClelland[57] note that the interaction of the unpaired electron with the nucleus of the cation is possible only in the ion pairs in contact, while in separated ion pairs this is prevented by the layer of solvent molecules. Hence the ESR spectra provide information about the concentration of the ion pairs in contact but not about the degree of dissociation of adducts into free ions[46,76].

The idea of the existence of two types of ion pairs has been used recently also to account for other phenomena in solutions of organometallic compounds of alkali metals. Thus Hogen-Esch and Smid[78] observed a change in the spectrum of fluorenylsodium solution in tetrahydrofuran at low temperatures. This phenomenon cannot be attributed to the formation of free ions, since the dissociation constant is very low — 4×10^{-5} M at 203°K. Therefore they concluded that a decrease of temperature is accompanied by the conversion of the ion pairs in contact into separated ion pairs, which have a different spectrum. According to Smid[75], separated ion pairs exist at room temperature in tetrahydrofuran solution of lithionaphthalene and ion pairs in contact in solution of sodionaphthalene in the same solvent.

Similar postulates were introduced recently by Szwarc[87,88] into the chemistry of living polymers to account for the effect of the solvent on the polymerisation kinetics. In his view, the active centres for the chain propagation of living polystyrene in tetrahydrofuran are separated ion pairs and in dioxan ion pairs in contact. Therefore in the first case the rate of polymerisation is about 200 times higher than in the second (the counter-ion is Li^+). Szwarc's explanation is satisfactorily consistent with McClelland's conclusion[57] that ion pairs in contact exist in solutions of metal adducts of benzophenone and anthracene in dioxan.

The mechanism of the dissociation of ion pairs represented by Eqn. (5) also explains satisfactorily[42,76,80] the shape of the curves for the temperature variation of the molar conductance of the adducts of aromatic hydrocarbons with alkali metals in ethereal solutions (Fig. 2). $\Lambda-T$ curves of similar shape were obtained by Hoijtink and coworkers[89,90] and Buschow[91] in studies on solutions of adducts of polyacenes in methyltetrahydrofuran. In particular, it was found that, as the temperature is reduced, the conductance of the lithium adducts falls rapidly, that of sodium adducts passes through a maximum, and that of potassium adducts increases slowly (in the case of potassiopentacene there is a maximum approximately about 220°K). The authors[89-91] explained these results by the increase of the dielectric constant of the solvent as the temperature is reduced, as a result of which the equilibrium in the dissociation of ion pairs is displaced towards free ions, and Λ increases. The simultaneous increase in the viscosity of the solvent lowers the mobility of the ions and results in a fall of Λ. Thus the shape of the $\Lambda-T$ curve is determined by the competing effects of two factors: the changes in the degree of dissociation and in viscosity.

† Recently Szwarc[85] examined quantitatively the problem of equilibria involving the participation of ions and ion pairs. He discussed the effect of the solvent on the degree of solvation, mobility, and association of ions, the structure of ion pairs, etc.

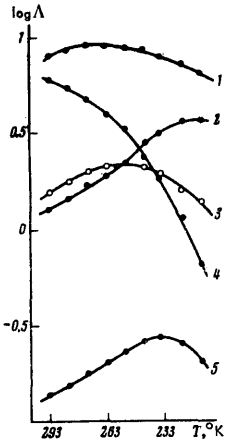


Fig. 2. Variation with T of log Λ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) tetrahydrofuran; 3) 1-ethoxy-2-methoxyethane; 4) dimethyl ether of diethylene glycol; 5) 1,2-diethoxyethane.

In conformity with the results of spectroscopic studies, Hoijtink and Buschow concluded that the effect of viscosity begins to influence Λ when the dissociation equilibrium is almost completely displaced to the right. They assert that lithium adducts are present in solution in the form of free ions even at room temperature, while complete dissociation of sodium and potassium adducts occurs at the temperature corresponding to the maximum value of Λ. However, when the effect of viscosity is removed by multiplying Λ by η, it is found that in almost all cases the conductance, and hence the degree of dissociation, increases continuously as the temperature is reduced, down to 213°K (Fig. 3). Comparison of the quantities $\Lambda_T\eta_T$ and $\Lambda_{293}\eta_{293}$ shows that at 213°K too the degree of dissociation is still far from unity. On this basis, one may conclude[80] that below a certain temperature, determined by the properties of the system under investigation, the effect of the increase in the viscosity of the solvent begins to influence Λ more than the increase in the degree of dissociation. Thus this, at first sight unusual phenomenon, can be rationally explained by taking into account the equilibria represented in Eqn. (5).

The heat of dissociation of ion pairs in contact into free ions $\Delta H'_d = \Delta H_1 + \Delta H_2$ is higher than the heat of dissociation of separated ion pairs $\Delta H''_d = \Delta H_2$. Hence it follows that the rate of change of the logarithm of the dissociation constant with $1/T$, which is $-\Delta H_d/R$, will be higher in the dissociation of ion pairs in contact. Probably it is because of this that at relatively high temperatures, when the concentration of ion pairs in contact is much higher than that of separated ion pairs, the effect of dissociation on Λ is more pronounced than the effect of viscosity, and Λ increases as the temperature is reduced. At lower temperatures, when the concentration of ion pairs in contact becomes insignificant and the increase of K_d is slower, viscosity has the dominant effect on Λ, and the latter falls, i.e. the $\Lambda-T$ curve passes through a maximum.

The above explanation presupposes that the temperature corresponding to the maximum value of Λ is the temperature at which one type of ion pairs is converted into the

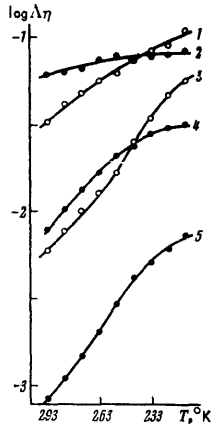


Fig. 3. Variation with T of $\log \Lambda\eta$ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) dimethyl ether of diethylene glycol; 3) tetrahydrofuran; 4) 1-ethoxy-2-methoxyethane; 5) 1,2-diethoxyethane.

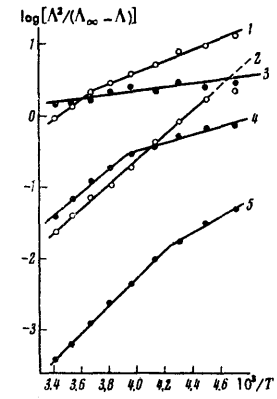


Fig. 4. Variation with $1/T$ of $\log [\Lambda^2/(\Lambda_\infty - \Lambda)]$ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) tetrahydrofuran; 3) dimethyl ether of diethylene glycol; 4) 1-ethoxy-2-methoxyethane; 5) 1,2-diethoxyethane.

other. The temperature (°K) of the transition of the sodionaphthalene ion pairs in contact into separated ion pairs falls with decrease in the solvating power of the solvent: dimethyl ether of ethylene glycol (> 293°) > 1,2-dimethoxyethane (273°) > 1-ethoxy-2-methoxyethane (253°) > 1,2-diethoxyethane (235°) > tetrahydrofuran (213°). The analogy with the temperature of conversion of one type of solvate of the sodium cation into another (p. 104) is striking. Possibly the formation of a coordination-saturated solvate is accompanied by the formation of separated ion pairs.

The existence of equilibrium between ion pairs in contact and separated ion pairs is confirmed by the calculation of the heats of dissociation (ΔH_d) of the adducts[42]. If the molar conductance at infinite dilution at any one temperature and the variation of Λ and η with temperature are known, it is possible to estimate approximately the variation of K_d as the temperature is reduced. Approximate values of ΔH_d were calculated from the slopes of the linear plots of $\log K_d$ against $1/T$. In agreement with the above explanation of the shape of the $\Lambda - T$ curves, the values of ΔH_d differ, depending on whether the molar conductance Λ increases or decreases as the temperature is reduced. In the first case $\Delta H_d \simeq$ -6– -9 kcal mole^{-1} and in the second $\Delta H_d \simeq$ -1.5– -4 kcal mole^{-1}. The higher value of ΔH_d is due to the dissociation of the ion pairs in contact. The available literature data on the heats of dissociation of adducts are close to those given above. Weissman[52] found from ESR spectroscopic data ΔH_d = -7.6 kcal mole^{-1} for sodionaphthalene in tetrahydrofuran and Smid[78] obtained from conductivity data ΔH_d = -8 kcal mole^{-1} in the range 298–253°K (ion pairs in contact) and ΔH_d = -1.5 kcal × × mole^{-1} below 253°K (separated ion pairs) for fluorenylsodium in tetrahydrofuran. Two values of ΔH_d correspond to the $\Lambda - T$ curves which pass through a maximum, and, as was to be expected, the lower value occurs at lower temperatures, where separated ion pairs predominate. Graphically this is reflected in a break in $\log K_d - 1/T$ plots (Fig. 4). The temperatures corresponding to the breaks and to the maximum values of Λ are approximately the same[80].

Ether	Break, °K	Maximum, °K
1,2-Dimethoxyethane	~273	~273
1-Ethoxy-2-methoxyethane	253	253
1,2-Diethoxyethane	235	238

The above considerations concerning the mechanism of the dissociation and the state of the adducts of aromatic hydrocarbons with alkali metals in ethereal solutions are in good agreement with the data on the solvating power of ethers of different structures. There is also agreement between the conclusion that two types of ion pairs exist (in contact and separated) and that the solvation of cations proceeds by a stepwise mechanism. It follows from the results of the study of the electrical conductivity of the ethereal solutions of naphthalene adducts that the interionic interaction, which determines the position of the dissociation equilibrium, depends significantly on the conditions of cation solvation.

IV. THE ROLE OF THE METAL AND SOLVENT IN RADICAL-ANION DISPROPORTIONATION AND REDUCTION EQUILIBRIA

The adduct of sodium and naphthalene, which is widely used to initiate anionic polymerisation[3–7], has a green colour whatever the ether in which it is formed; the green colour (absorption maxima at 365 and 810 nm) is due to the presence of naphthalene radical-anions. The reaction of naphthalene with lithium is different. In 1,4-dioxan and 1,2-diethoxyethane[45,92] the green colour of the radical-anions is appreciable only in the first instants after the solution of naphthalene comes into contact with the metallic lithium mirror (its preparation has been described by Petrov et al.[93]). A stable red colour is then obtained due to the appearance in the spectrum of a broad band at wavelengths near 550 nm. On addition of an excess of naphthalene to the red solution in the absence of lithium, this maximum disappears and the spectrum is then characteristic of the naphthalene radical-anions (Fig. 5). The above

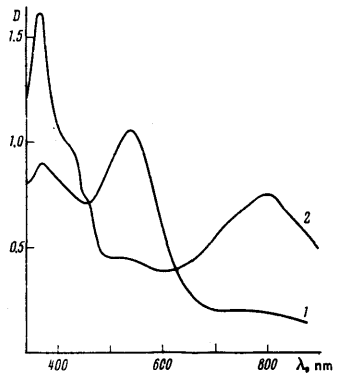


Fig. 5. Spectra of naphthalene–lithium adducts in 1,2-diethoxyethane:
1) in the presence of an excess of lithium; 2) in the presence of an excess of naphthalene.

phenomena have been interpreted[45,92] as evidence for the formation of naphthalene dianions. Their formation in the initial instants, when the solution still contains an appreciable amount of naphthalene, suggests that under these conditions they are formed as a result of the disproportionation of radical-anions [equilibrium (3)].

In tetrahydrofuran and 1,2-dimethoxyethane the green colour of the naphthalene radical-anions persists until reaction (1) involving the formation of radical-anions reaches completion. Only then does the colour of the solution change, and the broad band in the region of 550 nm appears in the spectrum. This means that in this case equilibrium (3) is displaced to the right and the dianions are produced preferentially by the reduction of radical-anions according to Eqn. (2).

Hoijtink and Buschow[94] were the first to describe the spectrum of the naphthalene dianions, which were obtained by the reaction of naphthalene with lithium in methyltetrahydrofuran. They noted that the dianions, which are very reactive, are readily protonated by the solvent at room temperature, forming the carbanions ArH^-:

$$C_5H_{10}O + Ar^{2-}2M^+ \rightarrow ArH^-M^+ + C_5H_9O^-M^+. \quad (6)$$

For this reason, it was impossible to obtain the spectrum of the dianions without the superposition on the latter of the spectrum of the carbanions, which absorb in the wavelength range 350–500 nm.

Smid[75] quotes the spectrum of the solution of the products of the reaction of lithium with naphthalene in tetrahydrofuran (absorption maximum of the dianions at 555 nm), which is of a very similar form to that measured by Shatenshtein et al.[92]

Henrici-Olivé and Olivé[95-98] studied the properties and the preparation of solutions of naphthalene dianions in tetrahydrofuran. They investigated the reactions of lithium and sodium with naphthalene in dimethoxyethane and tetrahydrofuran by measuring the magnetic properties of the solutions of the resulting adducts. They observed that in tetrahydrofuran in the presence of an excess of lithium the concentration of the paramagnetic adduct is much lower than the initial concentration of the hydrocarbon, while the active alkalinity (determined by titration with propyl alcohol) is 1.5 times greater than the alkalinity corresponding to the complete conversion of naphthalene into radical-anions (in 1,2-dimethoxyethane and also with sodium in tetrahydrofuran such phenomena were not observed). Hence Henrici-Olivé and Olivé concluded that, in the presence of an excess of lithium in tetrahydrofuran, dianions are formed together with radical-anions. According to these investigators[96], about 90% of the naphthalene is converted into dianions in 5 h (ratio of the number of lithium gramme-atoms to the number of moles of naphthalene 4.5; concentration of naphthalene 0.15–0.2 M). The colour of the solution gradually changes from green to dark violet. As was to be expected, the addition of an excess of naphthalene to the solution of the dianions results in the restoration of the green colour and an increase in the paramagnetism of the solution.

There exists a definite relation between the state of the adduct in solution and the mode of formation of the dianions, namely the disproportionation of the radical-anions occurs more readily in those solvents where the adducts are present predominantly in the form of ion pairs in contact, since, according to Garst[77], the powerful interionic attraction in such pairs favours the disproportionation reaction, compensating the energetically unfavourable repulsion of electrons in the dianions. On the other hand, if the adduct (lithionaphthalene) is present in solution in the form of separated ion pairs, the electrostatic interaction between the ions is weaker and the disproportionation virtually does not occur. The reduction of the radical-anions as well as their formation according to Eqn. (1) are favoured by solvents with a higher solvating power, in which separated ion pairs are present.

The problem of the disproportionation reactions has been considered in greatest detail by Garst[75,79,100] from the above standpoint. In the study of the effect of the solvent on the radical-anion disproportionation equilibrium it was found that the disproportionation constant (K_{disp}) of sodiotetraphenylethylene[99] increases in the series dimethyl ether of diethylene glycol $\simeq$ 1,2-dimethoxyethane $<$ tetrahydrofuran $<$ 1,4-dioxan, ethyl ether. The following sequence of solvents as regards their effect on the disproportionation constant of sodiostilbene has been obtained[100]: tetrahydrofuran $<$ methyltetrahydrofuran $<$ 1,4-dioxan. After comparing these data with the shifts in the spectra of sodiobenzophenone ketyl as a function of the solvent[55], Garst concluded[99] that a decrease in the degree of solvation of ions (mainly the cations) favours the displacement of the equilibrium in the direction of the formation of dianions. When the temperature is reduced, the degree of solvation of the cations increases, and the interionic attraction weakens, as a result of which the equilibrium should be displaced towards the formation of radical-anions, as is observed experimentally. The increase of the constant K_{disp} for the radical-anions of tetraphenylethylene in tetrahydrofuran with increase in the radius of the cation (at room temperature) observed by Garst and Zabolotny[77] and Ewans and Tabner[101] does not contradict this explanation either, since the interionic interaction in the above solvent increases in the series of cations $Li^+ < Na^+ < K^+$. At the same time Garst et al.[99] observed that in methyltetrahydrofuran, whose solvating power is lower than that of tetrahydrofuran, K_{disp} for stilbene radical-anions decreases in the opposite sense compared with tetrahydrofuran, i.e. with increase in the radius of the cation. Garst[77] believes that this reversal of the reactivity of metals is caused by competition between interionic interaction and solvation. If the reaction is performed in a solvent which solvates cations to a high degree, then the

solvation effect predominates as the radius of the cation increases, and K_{disp} falls, while in a weakly solvating solvent the effect of interionic interaction prevails and K_{disp} increases with the radius of the cation. Thus the dianion formation reactions also convincingly demonstrate the close relation between the phenomenon of cation solvation and interionic interaction (see also Refs. 102 and 103).

It must be emphasised that the above relations involving the effect of the solvent and the nature of the alkali metal on the formation and ionic dissociation of the adducts of alkali metals with aromatic hydrocarbons are of a more general significance, since they apply to a considerable extent to the entire field of organic anionic reactions. To illustrate this postulate, one may refer to the reviews published in this journal[104,105] and to the work carried out in our laboratory[73,106-111] on a series of anionic reactions in ether solvents.

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MODERN IDEAS ON THE SUPERMOLECULAR STRUCTURE OF CELLULOSE

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According to modern ideas, cellulose macromolecules form long, unbranched, elastic threads, consisting of D-glucopyranose residues linked by β-glucoside bonds in the 1,4-position.

Since each glucopyranose residue contains alcoholic hydroxy-groups, the cellulose molecule with a degree of polymerisation of 1000 contains 3000 hydroxy-groups. These groups screen the adjacent units in the cellulose macromolecule, and are responsible for rigidity and elasticity; they also determine the nature of the bonds between the macromolecules. The way in which the cellulose macromolecules are mutually arranged in natural and synthetic fibres and in films has an important effect on the strength, stretch, elasticity, hygroscopicity, reactivity, solubility, capacity to undergo wet grinding, ability to take dyes, and many other properties of these fibres.

Unfortunately, we still know very little about the supermolecular structures that are responsible for these properties of cellulose. Nevertheless, it is in this field that we must look for an explanation of processes that lead to the preparation of ultra-strong cellulose fibres, highly reactive celluloses, and other materials of great industrial importance.

Numerous electron microscope studies of natural cellulose fibres carried out in the last 10–15 years have shown that these have a fine fibrillar structure, the diameter of the elementary fibrils varying from 70 to 150 Å, depending on the origin of the preparation [1-5]. However, it has recently been shown that, in an aqueous medium, the microfibrils of some samples of natural cellulose can be cleaved by ultrasonic vibrations into smaller microfibrils with a diameter of about 35 Å. [6,7]

The structure of artificial cellulose fibres depends on a number of factors, the most important being the degree to which they are drawn [8,9]. The more the hydrocellulose fibres are drawn during their formation, the more well defined is their fibrillar structure. X-Ray and electron diffraction studies of natural fibrils suggest that these are made up of macromolecules, arranged parallel to and along the fibril [1,4].

Ranby and other workers have shown that, when natural or regenerated cellulose is subjected to mild heterogeneous hydrolysis, the microfibrils do not react in a uniform manner along the main axis [10,11]. It would appear that the microfibrils are constructed of continuously alternating sections that differ in the rate at which they are hydrolysed. After the readily hydrolysable sections have been dissolved, the microfibrils are broken up by ultrasonic vibrations into short spindle-shaped fragments. The average length of the cellulose macromolecules in these particles, or "micelles", as Ranby calls them, measured in the electron microscope, is about the same as the average length of cellulose residues determined by viscosimetric, diffusion, or sedimentation methods.

This made it possible to evaluate the length of the sections of the cellulose macromolecule that are difficult to hydrolyse from a knowledge of the average degree of polymerisation of the residue after hydrolysis (limiting degree of polymerisation), which was determined from the viscosity of solutions of nitrates or copper complexes [12-22]. The size of the sections of the microfibrils that are difficult to hydrolyse is not constant and depends on the origin of the cellulose sample. Thus, observations with the electron microscope have shown that, after mercerisation or regeneration of cellulose from solution, the length of the microfibrils that are difficult to hydrolyse is reduced by a factor of 2–4. [10,11]

Studies on the limiting degree of polymerisation have shown that there is a great difference in supermolecular structure between natural and artificial cellulose fibres. The limiting degree of polymerisation of wood cellulose is 400, [23] but in cord fibres of viscose origin this value varies between 40 and 20.

It is interesting that, in the preparation of ultra-strong fibres, the degree of polymerisation decreases instead of increasing, as might be expected [24,25]. A similar phenomenon is observed in the decomposition of viscose in a precipitation bath with an increasing content of salts [26]. This example shows that in nature cellulose is formed with large sections that are difficult to hydrolyse, but in the preparation of artificial hydrocellulose fibres these sections are 1/10 to 1/20 the size of the natural sections.

Studies carried out in recent years have shown that the readily hydrolysable sections of cellulose macromolecules undergo oxidation [27], thermal decomposition [18,28], enzymic hydrolysis [29], and alcoholysis [30] much faster than the other sections.

Using the electron microscope, Hess and coworkers showed that, after treatment with iodine, the microfibrils are not uniformly stained, and alternating dark and bright sections are formed [31]. In size the bright sections were similar to Ranby's micelles that were difficult to hydrolyse. It was concluded that the dark sections containing iodine are readily accessible amorphous components of cellulose.

Similar lack of uniformity in these microfibrils was observed by Manly, who subjected the fibrils to preliminary treatment with an aqueous solution of uranyl acetate or phosphotungstic acid [7]. After this treatment, the microfibrils of the Valonia algae showed the presence of a "bead-like" structure, with individual oval-shaped beads, 175 Å wide and 200 to 400 Å long. Dark coloured connective tissue was present between these formations. The microfibrils of ramie, cotton, and wood cellulose 35 Å in diameter, obtained after vigorous treatment of larger microfibrils with ultrasonic vibrations, also had a bead-like structure. Manly has suggested that this periodicity along the microfibril axis might be due to the formation of the fibril from a band folded into a spiral. However, sufficient evidence to support this has not been obtained, because the measurement is at the limit of the resolving power of modern electron microscopes, and the use of ultrasonic vibrations might lead to further profound structural changes.

It has been shown that the easily hydrolysed fraction of cellulose is hydrolysed 50–60 times more rapidly than the fraction that is difficult to hydrolyse [32]. But there is no sharp transition between these two fractions; this has led some workers to suggest that there is an intermediate mesomorphic cellulose fraction that is hydrolysed at a rate between the rates for the two extreme fractions [14].

It has recently been shown that the density of the cellulose fraction that is difficult to hydrolyse is much greater than that of the easily hydrolysable fraction, and this density varies with the type of cellulose [33,34].

It was also found that the rate of heterogeneous hydrolysis or alcoholysis of the fraction difficult to hydrolyse decreased as the density increased [33,34]. Measurement of the true specific gravity of cellulose during hydrolysis showed that the easily hydrolysed fraction becomes somewhat more dense and its reactivity decreases [35]. This effect is due to the rupture during hydrolysis of strained sections of the macromolecule with the formation of a denser structure.

The increase that occurs in the density of cellulose in the presence of water has been studied from several points of view. It has been shown that cellulose regenerated from its derivatives, for example, the acetate [36] or the xanthogenate [26], generally forms a loose low-density structure that readily undergoes ethanolysis and hydrolysis. When moistened with water, these types of cellulose rapidly become more dense and less reactive.

An especially large density effect was observed when loose cellulose obtained by dry grinding in special mills was moistened with water [37-40].

In recent years the use of alcoholysis [30,35,38-42] and dioxanolysis [35,43] instead of hydrolysis has facilitated studies on the increase in density of reactive cellulose. This change in methods of cleaving cellulose has to a great extent reduced its tendency to increase in density and so has limited the distorting effect of density increase on the quantitative determination of the portion of cellulose that reacts easily [35,38] and also of the maximum degree of polymerisation [44]. As the same time the use of hydrolysis and

alcoholysis in the investigation of various cellulose samples enabled a quantitative study to be made of the spontaneous increase in density that occurs when cellulose is cleaved in polar liquids[23-35].

As mentioned above, the cellulose macromolecules in natural and artificial microfibrils form alternating dense and loose sections along the main axis; this variation appears to be due to the tendency of the long cellulose macromolecules to undergo mutual orientation when highly swollen structures are dehydrated and their orientation is destroyed. The sections of the macromolecule between the dense, oriented sections must cause mutual lack of uniformity in the arrangement of the chains, and this must be reflected in the formation of looser, less oriented, structures in these sections, which are therefore more accessible to reagents. It is quite possible that the size of the oriented and of the loose sections along the microfibril depends on the initial orientation of the macromolecules produced under the conditions of formation of the sample. The greater the orientation in the initial swollen sample, the greater will be the tendency to form dense, highly oriented (crystalline) sections instead of sections with a loose (amorphous) structure, and vice versa.

Studies on the limiting degree of polymerisation of various cellulose samples have shown that the size of the dense, oriented, and more reactive sections depends on the method and conditions of regeneration of the cellulose[26]. Thus, for example, the presence in the precipitation bath of sodium sulphate, zinc sulphate, and especially of modifiers, promotes the preparation from viscose of cellulose with a large number of loose sections and small dense, oriented sections. The double-bath method of regenerating cellulose enhances this effect still further.

On the other hand, stretching increases the proportion of the less reactive fraction by increasing the proportion of oriented sections in the macromolecules[35]. This effect is still further increased by the swelling of hydrocellulose fibres, for example, in aqueous alkali[44]. Thus, the size of the dense and loose sections in cellulose depends on the origin of the cellulose and can be controlled within certain limits.

A study of the stability of fluctuations along the microfibrils of cellulose is of great interest. Recently this process has been elucidated using a method in which hydrogen of the hydroxy-groups in cellulose is exchanged for deuterium or tritium.

It had previously been shown that, when cellulose is immersed in heavy water, the hydrogen of the hydroxy-groups in the loose sections of the molecule is readily exchanged for deuterium[45,46].

Under these conditions, the hydrogen of the hydroxy-groups of the dense sections is not exchanged. To determine the mobility of this equilibrium, Sepall and Mason[47,48] repeatedly moistened cellulose samples with deuterium oxide or tritium oxide, drying them after each immersion. They found that, after 100 to 200 treatments, virtually all the hydrogen atoms of the cellulose hydroxy-groups had been exchanged for deuterium or tritium; the proportions of dense and loose sections of the macromolecule remained constant. With a single treatment, deuterium and tritium became inaccessible after penetrating into the densely packed sections of the macromolecule and were not exchanged for ordinary hydrogen.

According to Sepall and Mason, this observation indicates that fluctuations in the macromolecules in the microfibrils are not constant, and when the cellulose is alternately moistened with water and dried, the dense and loose sections in the microfibrils can be displaced along the fibril axis. It is interesting that the rate of replacement of hydrogen in the densely packed sections increases with the degree of swelling of the cellulose and with the temperature of the water.

Thus, the periodic increases in density in the bundles of cellulose macromolecules described above are not stable.

The nature of the bonds between adjacent macromolecules is of particular interest from the point of view of the supermolecular structure of cellulose. As early as 1926, Slonsler and Dore and then Higgins and Park advanced the hypothesis, on the basis of analogies with other compounds containing hydroxy-groups, that the hydroxy-groups of adjacent cellulose macromolecules form hydrogen bonds. But it was not until 1940 that Ellis and Butt[49] showed by means of infrared spectroscopy that all the hydroxy-groups of cellulose are in fact linked by hydrogen bonds. This conclusion was later confirmed by many workers and it is now fully accepted.

It must, however, be borne in mind that a small proportion of the hydroxy-groups, situated on the external and internal surfaces of cellulose fibres or films, must remain free for reasons of geometry. Direct estimation of these free groups with CH_3MgI in ethyl ether by Tserevitinov and Chugaev's method shows that the number of free hydroxy--groups in cellulose fibres accessible to the Grignard reagent is 5% of the total number of groups[50]. The remaining hydroxy-groups appear to be linked by intramolecular or intermolecular hydrogen bonds. The energy of these bonds varies from 2–3 to 6–7 kcal $mole^{-1}$, and it depends on the spacing between the groups and on steric hindrance.

The closer are the hydroxy-groups of adjacent cellulose macromolecules the stronger are the hydrogen bonds between them. For this reason, the thermodynamic method should be the best method for evaluating the bonding energy of adjacent molecules in a unit volume of cellulose. Unfortunately, such methods are not yet available, and the strength of the hydrogen bonds must therefore be measured by an indirect method. Infrared spectra are most generally used for this purpose.

The vibrations of free alcoholic hydroxy-groups correspond to an absorption maximum at 3570–3580 cm^{-1}. When hydrogen bonds are formed between the hydroxy-groups, absorption bands appear in the 3550–3000 cm^{-1} region, and the stronger the hydrogen bond the greater is the deviation from the absorption band of free hydroxy-groups. Examination of the spectra obtained shows that cellulose preparations give a broad set of absorption bands in the hydrogen--bond region[51]. This indicates the presence of hydrogen bonds of different strengths, which are responsible for the properties of the given type of cellulose. It is therefore possible to characterise the hydrogen bonds between the macromolecules by measurements based on indirect properties, such as the ability of certain reagents to penetrate deeply into the cellulose and rupture these bonds.

The most widely used and the simplest method of this kind is the determination of the absorption of water from air at a definite relative humidity. The ratio of the amount of moisture absorbed by the cellulose to the amount of moisture absorbed under the same conditions by cotton cellulose is termed "accessibility". It has been shown that the value of this accessibility depends on the structure of the cellulose and is independent of the relative humidity of the air[52].

Since, in air of low relative humidity, absorption of water is due to binding by alcoholic hydroxy-groups of the cellulose on the accessible surface of the sample, the quantity of water absorbed is a measure of the area of this surface. Here it must be borne in mind that water molecules that penetrate into the capillaries of the cellulose can break weak hydrogen bonds and penetrate into the depth of the cellulose, causing it to swell. Thus, it should be noted that the term "accessibility", measured by absorption of moisture, refers not only to the surface of the dry sample, but also to the surface that is formed as a result of swelling[53-57].

X-Ray studies have shown that water is absorbed by the loose part of the cellulose and does not penetrate deeply into the tightly packed sections of the macromolecules.

Methods of measuring the swelling of cellulose and in particular its dissolution are widely used in determining the intensity of intermolecular interaction in cellulose. These methods are based on the hypothesis that the most weakly bound macromolecules are the first to pass into solution. For the differential evaluation of the strength of the hydrogen bonds, methods are used in which the cellulose preparations under test are treated with solvents of gradually increasing dissolving power. This enables an arbitrary spectrum of bond strengths to be determined for different cellulose preparations[58].

However, the increase in the solubility of cellulose when its degree of polymerisation is reduced must be taken into account; intermolecular interaction is obviously no less decisive.

The methods to be considered here include those based on the swelling and dissolution of cellulose in ethylenediamine and its complexes, in cuprammonium solution, in solution of iron tartrate complex, in aqueous solutions of alkalis, sodium zincate, quaternary ammonium bases, calcium thiocyanate, chloral hydrate, zinc chloride, concentrated sulphuric acid and phosphoric acids, etc.[59-67].

Important results have also been obtained by measuring the rate of reaction of cellulose under heterogeneous conditions. Thus, for example, Nickerson and Troitzsch and other workers[68,69] used a method in which cellulose was partially formylated with formic acid of different concentrations at different temperatures.

In 1953 the present author in collaboration with Korol'kov and Garmanova[70] used the oxidation of cellulose with nitrogen dioxide, in the gaseous state or dissolved in carbon tetrachloride, for this purpose; this method was also used later by Roseveare and Spaulding[71]. Hydrolysis, ethanolysis, etc. may also be mentioned here.

Attempts have been made to evaluate the strength of the bonds between the macromolecules by measuring the amount of heat evolved in the mercerisation of cellulose by alkali solutions of increasing concentration[58], and also from the changes in the X-ray diffraction pattern of cellulose (as a result of the transition from cellulose I to cellulose II) after treatment with such solutions[72,73], and by measuring the rate of decrease of the degree of polymerisation of cellulose subjected to mild hydrolysis[74], etc. By means of these methods, data were obtained characterising the degree of lateral order in the whole mass of cellulose, that is, in the dense and loose regions.

To determine the degree of lateral order in the dense sections alone, some workers treated the cellulose in two stages; the first consisted of mild hydrolysis or ethanolysis to destroy loose regions, and in the second stage the residue was dissolved in aqueous solutions of sodium hydroxide of increasing concentration[75,76].

The methods enumerated above have been used to evaluate the heterogeneity of the energy of the lateral bond in various cellulose preparations and the variations have been represented on histograms. These methods have recently been used to characterise cellulose.

However, the heterogeneity of cellulose fibres due to their different anatomical structure must also be taken into account, and also heterogeneity due to compounds associated with cellulose which affect its solubility and tendency to swell.

The elucidation of the phase diagram of cellulose is of particular interest. At present the most widely held view is that cellulose consists of two phases, an amorphous and a crystalline phase; the amorphous phase is identified with the loose, readily accessible portion of cellulose, and the crystalline phase with the dense, oriented portion, which has a low reactivity. Such an interpretation applied to a polymer is usually associated with the presence of an interface between the two phases. It should, however, be noted that the presence of this interface has still not been demonstrated, and it is unlikely that such an interface exists. In this connection, many workers consider that cellulose may be partly in the mesomorphic or transition state; this state is characteristic of the boundary region between the amorphous and crystalline sections. Mark, in a typical statement, classifies cellulose as a stereoregular polymer, the rigidity of these polymers being due to the rigidity of the glucopyranose rings themselves and to strong intermolecular bonds[77]. When the molecules are arranged parallel to one another, these bonds promote the formation of crystal-like packets or aggregates. The terms "crystallite" and "crystallisation" are used with reference to certain regions within the cellulose system that show a state of three-dimensional order similar in some respects to the order in crystals of ordinary low-molecular compounds, such as sucrose, maleic anhydride, etc. However, the crystalline regions in cellulose do not have the regular shapes characteristic of ordinary crystals. They are much smaller and they are much more defective. Here the crystalline regions are linked with the non-ordered, amorphous regions by chains passing through both regions. Thus, there is no sharp boundary between the ordered (crystalline) regions, in which the molecules are arranged parallel to one another, and the non-ordered (amorphous) sections. Many workers share the view that cellulose is a single-phase crystalline system with a large number of dislocations[78]. In isolated sections of such a structure, the incidence of defects may be so great that the compound in these sections can be regarded as amorphous. In natural microfibrils highly oriented and poorly oriented sections regularly alternate along the length of the fibril, forming a bead-like structure. As mentioned above, the proportions in which these sections are present depend on the origin of the sample.

The alternation of sections differing in orientation is also found in regenerated cellulose, which does not have a microfibrillar structure, but here the regularity is less marked.

The variations mentioned in the structure of cellulose are similar among themselves and are based on the general idea that defect crystalline structures are present in cellulose.

Numerous X-ray structure studies on cellulose, especially those carried out in recent years[79-81], have definitely confirmed that cellulose contains three-dimensionally ordered regions with unit cells of fixed dimensions.

The degree of mutual orientation of cellulose macromolecules, measured by X-ray diffraction, varies within wide limits in different samples of cellulose. According to Ranby's studies, this orientation reaches a high degree in animal and bacterial cellulose and gradually decreases in cotton, and particularly in wood cellulose (Fig. 1).[82] Crushing and, in particular, dry grinding reduces the degree of orientation of natural cellulose[39,83,84].

The degree of orientation of highly stretched hydrocellulose fibres is much greater than that of isotropic fibres. However, the intensity of interaction (hydrogen bonds) between the macromolecules of natural and regenerated cellulose differs greatly, as is indicated by variations in the tendency to swell and to dissolve. The interaction between the macromolecules in natural fibres is much stronger than that in artificial fibres. For example, the solubility of natural cellulose in 10% aqueous sodium hydroxide solution generally does not exceed 10–20%, but under the same conditions regenerated cellulose in the form of fibres or films dissolves to the extent of 40–90%.

The energy of the interaction of macromolecules in "polynose" fibres is much greater than that in ultra-strong cord fibres. The difference in the packing of macromolecules is also displayed in a number of other properties. For example, natural cellulose has a higher density (1.55–1.60) than hydrocellulose fibres or films (1.495–1.530),[35] and it is hydrolysed[85-86] and ethanolysed[33] more slowly.

The special features of the supermolecular structure of cellulose mentioned above confirm that modifications of this structure exist with high bond energy (natural fibres) and low bond energy (hydrocellulose fibres). Each modification may show a different degree of mutual orientation of its macromolecules. The X-ray diffraction patterns of these two basic types of cellulose are different, which indicates a difference in the spatial arrangement of the macromolecules in a three-dimensional lattice. These two types of cellulose have been named cellulose I and cellulose II.

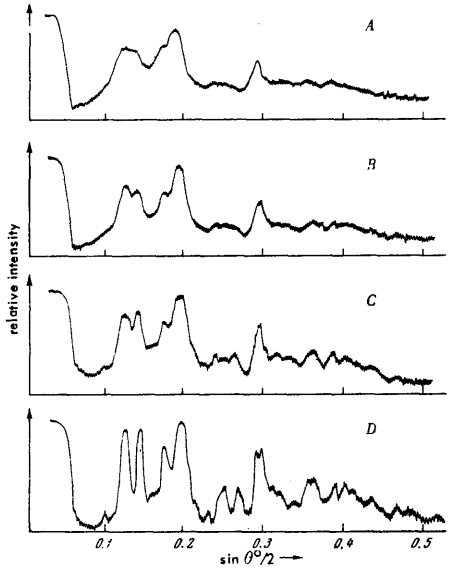


Fig. 1. X-Ray powder diffraction patterns of natural cellulose of different origins:
A) wood cellulose; *B*) cotton cellulose; *C*) animal cellulose (tunicine); *D*) cellulose from valonium algae[82].

It should be noted that this division of cellulose according to the strength of the side bonds and the structure of the unit cell is somewhat arbitrary, since cases are known in which there is a relatively strong side bond in cellulose II (for example, in "polynose" fibres).

At present, cellulose III and cellulose IV[87-88] are also known, the latter being formed from cellulose II by heating. In older papers reference was made to the conversion of cellulose II into cellulose I under these conditions, but this has not been confirmed by later studies[87,88]. A new, fifth modification of cellulose (cellulose X) has recently been described[89,90].

The unit cell of natural cellulose, or cellulose I, has been most studied[89,91-96]; this cell is monoclinic and has the following dimensions: a = 8.35 Å; b = 10.3 Å; c = 7.9 Å; angle β = 84°; volume 672 Å^3.

Wellard[97], who recently studied a large number of different natural celluloses, showed that the dimensions of their unit cells vary within comparatively narrow limits. Mercerised natural and highly oriented regenerated cellulose have the monoclinic cell of cellulose II with the following dimensions: a = 8.02 Å; b = 10.3 Å; c = 9.03 Å; angle β = 62.8°.[91-96,98-100]

Cellulose III is obtained by treating natural cellulose with non-aqueous liquid ammonia[101,102] or ethylamine[103]. Its unit cell has the following dimensions: a = 7.74 Å; b = 10.3 Å; c = 9.90 Å; angle β = 58°.

Cellulose IV, which is obtained by heating cellulose II in water or glycerol at high temperatures[87], has a unit cell of the following dimensions: a = 8.12 Å; b = 10.3 Å; c = 9.03 Å; angle β = [value omitted in Russian original (Ed. of Translation)].

Cellulose X, a new modification that has been little studied, was obtained by the regeneration of natural cellulose from its solutions in 40.3% hydrochloric or 85% phosphoric acid[89,90].

It is of interest to note that cellulose III is the only modification that can be converted into the initial natural cellulose I; up to now celluloses II, IV, or X have not been converted into cellulose I.[104]

All these modifications of cellulose give different X-ray diffraction patterns (Fig. 2); this appears to be due to differences in the configurations of the unit cells[91-96].

Thus, polymorphism is observed in cellulose. It is of interest that cellulose I is the only cellulose formed in nature, and has not yet been prepared in the laboratory.

The crystalline nature of cellulose has been demonstrated in different samples by studies on double refraction[105,106], magnetic anisotropy[107], fluorescence[108], and the piezoelectric effect[109-111].

The crystalline structure of highly oriented cellulose is indicated by the splitting (dichroism) of the absorption bands in the infrared spectra[112], and also by the X-ray diffraction patterns of true crystals of oligosaccharides obtained by the

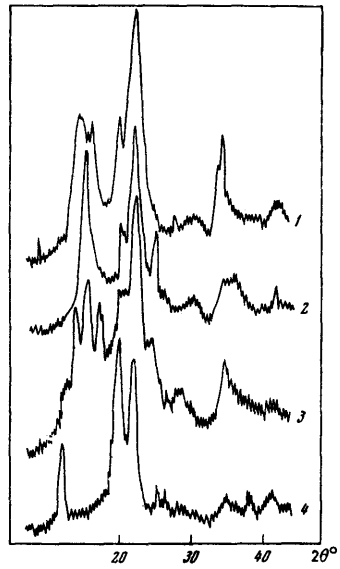


Fig. 2. X-Ray powder diffraction patterns of various modifications of cellulose:
1) cellulose I; 2) cellulose IV; 3) cellulose X; 4) cellulose II; the absorption intensity is plotted on the ordinate and the double angle (2θ) on the abscissa.[96]

extensive cleavage of cellulose (from cellulose to cellohexaose). In the latter case, after acetolysis of the cellulose and subsequent chromatography on a celite column, well crystallised oligosaccharides with a degree of polymerisation between 2 and 7 were separated[113]; these were identified after saponification. Oligosaccharides with a degree of polymerisation of 4 or more showed X-ray diffraction patterns virtually identical with the patterns of cellulose II. Thorough chromatographic separation of the oligosaccharides ensured that compounds of longer chain length did not appear in these fractions. Thus, typical crystals of higher oligosaccharides of cellulose obtained from aqueous solutions gave X-ray diffraction patterns characteristic of one of the modifications of cellulose that is also only formed in the presence of water (cellulose II).

The X-ray diffraction method, which shows the presence of regions of varying degree of orientation in cellulose, is widely used for the qualitative and quantitative evaluation of the extent to which cellulose occurs in the crystalline form[95,114-117].

It should, however, be noted that this method of quantitatively evaluating the crystallinity of cellulose is to a large extent arbitrary and should be used with great caution. For example, comparison of the X-ray diffraction patterns of hydrocellulose fibres[118] before and after removal of the easily hydrolysed (amorphous) fraction showed that the fibres contained virtually the same amount of "crystalline" fraction, although the proportion of the crystalline fraction would be expected to increase greatly after hydrolysis. It has been reported in other papers, however, that a slight increase in the proportion of crystalline fraction is observed when various celluloses are subjected to mild hydrolysis[119].

Various physical and chemical methods have been used in determining the degree of crystallinity of cellulose. Some of these are based on the removal of the amorphous fraction by hydrolysis with dilute acids[120-125], or by oxidation with periodic[26] or chromic[126] acids. In other methods the degree of crystallinity is determined from the absorption of water[127,128], from the rate of exchange of hydroxy-group hydrogen atoms for deuterium[45,46], or tritium[47,48], from the density of the crystalline and amorphous sections[106,129], from the heat of wetting[130], from the absorption of iodine from aqueous solutions[131,132], and from the exchange of hydroxy-group hydrogen atoms of the amorphous sections for thallium in solutions of thallium ethoxide[133], or for sodium in solutions of sodium in liquid ammonia[134].

Methods based on differences in the rate of esterification of the amorphous and crystalline fractions of acetylation[135] or formylation[136-138] form a separate group.

It should be noted that none of these methods gives a clear idea of the degree of crystallinity; they merely indicate the density of packing, the degree of orientation, and the strength of intermolecular bonds; this must be taken into account in the evaluation of the results obtained. Thus, at present we have no reliable methods for determining the degree of crystallinity of cellulose.

This is obviously due, firstly, to the absence of a clear boundary between the crystalline and non-crystalline sections, and, secondly, to the failure of many workers to distinguish properly between "crystalline" and "dense" sections; not all densely packed sections and sections difficult of access can be regarded as crystalline.

Of the methods enumerated above, the X-ray diffraction method appears to be the most suitable for determining the crystallinity of celluloses, but even this method must be used with great caution.

Another point of view on the phase state of cellulose is based on the hypothesis that it has an amorphous structure. Kargin is the founder of this theory in the Soviet Union. Over a period of many years, he and his students have systematically supported and advocated the theory that cellulose is an amorphous polymer with an anisotropic structure[139-149]. He considers that clear X-ray diffraction patterns obtained on a number of vegetable fibres have been incorrectly evaluated by some workers as providing proof of the crystalline structure of the polymer. According to Kargin and coworkers, it is necessary to distinguish between the elements of order responsible for the mutual arrangement of the chains and the order that arises on crystallisation of the polymer[146]. In the latter case additional bonds are formed without substantial change in the order of the arrangement of the macromolecules, but the proportion of these bonds is not great compared with the degree of order in oriented samples.

To determine the phase composition of cellulose, Kargin and coworkers used a method based on the dependence of the interference width on the wavelength of the beam used in systems with long-range order. For this purpose, they studied the interference obtained by the reflection of X-rays (wavelength 1.54 Å) and an electron beam (wavelength 0.05 Å). Since they found no such dependence, they concluded that cellulose has an amorphous structure.

Unfortunately, the electron diffraction method as applied to cellulose has serious disadvantages, and for this reason the results obtained have been criticised by some workers[81].

Evidence in favour of the amorphous structure of cellulose is also provided by the change that occurs in the X-ray diffraction pattern of an isotropic viscose film when the latter is stretched. It has been shown that, when signs of

a high degree of orientation of the film appeared in the X-ray patterns, there were no new interferences that could be ascribed to the crystallisation of the cellulose [141]. These experiments confirm that no phase transition from the amorphous to the crystalline state occurs, provided that these two states show different interferences, which has not yet been confirmed.

In this respect, the changes in X-ray interferences in natural and highly oriented, artificial cellulose fibres that have been subjected to dry grinding are interesting. Under these conditions, it is characteristic that the interferences in the natural cellulose entirely disappear (Fig. 3) without new ones appearing [39,83,84], although the cellulose retains most of its properties (transition to the amorphous state). When ground cellulose from highly oriented viscose fibre is treated with water, the initial X-ray diffraction pattern of the fibre is partly restored.

In developing the theory of the amorphous structure of cellulose, Kargin et al. attempted to change the second-order transition temperature of cellulose, that is, the transition point at which it changes from the vitreous to the highly elastic state, by the introduction of plasticising additives [145]. Under these conditions, the amorphous polymers show a reduction of the second-order transition temperature. Experiments in which triethylphenylammonium hydroxide was added as a plasticiser to cellulose confirmed that this transition temperature is reduced; it was therefore concluded that cellulose always exists in the vitreous state.

By measuring the integral heats of solution in triethylphenylammonium hydroxide of cellulose fibres with differing degrees of orientation, Mikhailov and Fainberg attempted to show that these fibres undergo a phase transition [150]; no appreciable difference in the heats was observed. This was interpreted as demonstrating that cellulose was amorphous in all the samples examined.

In 1962 these workers determined the heat capacity of isotropic and highly oriented cellulose fibres and observed no appreciable difference; this was also interpreted as proof that cellulose is amorphous [151].

The experimental results mentioned above obtained by Kargin and his students led them to conclude that cellulose fibre is a body that is solid in its state of aggregation but liquid in its phase state, with oriented anisodiametric molecules. Therefore, cellulose fibre is an anisotropic liquid phase the equilibrium state of which corresponds to a completely disoriented structure. Under normal conditions this process [attainment of equilibrium (Ed. of Translation)] is inhibited by the existence of a fixed structure [144].

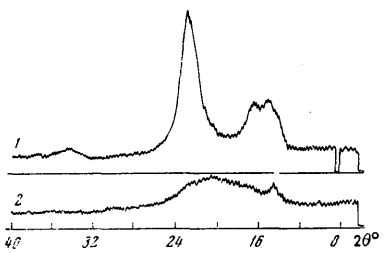


Fig. 3. X-Ray powder diffraction patterns of natural cotton cellulose before (1) and after (2) dry grinding.[39]

In later work Kargin and coworkers studied the supermolecular structure of viscose ultra-strong cord fibres and observed that these contained "ordered structural forms", which, however, were not internally perfect [152]. This indicated that cellulose undoubtedly shows a high degree of order. This interpretation that cellulose has an amorphous structure with a high degree of order agrees with the interpretation previously advanced that in amorphous cellulose the unfolded chains form packets (clusters), with isolated macromolecules passing through several packets.

These considerations are largely in agreement with modern views on cellulose accepted by advocates of both the crystalline and the amorphous hypotheses. The differences between the advocates of the two hypotheses appear to be mainly differences in terminology, the physical interpretations being very similar.

Now the main question in dispute is what name should be given to the "packet", which is recognised by all: should it be regarded as a crystal or as a highly oriented amorphous formation? Discussions in Soviet journals have shown that at present this question cannot be unambiguously answered because of the absence of reliable methods of investigation [78,154-159].

A final decision can probably only be reached by a study of an artificial cellulose crystal, with well defined boundaries, that can be assigned to a definite crystallographic system. If such a crystal had a diffraction pattern and other properties similar to those of highly oriented natural and regenerated cellulose, this would indicate that cellulose has a crystalline structure; on the other hand, if these properties were different, the crystallinity of cellulose would not be demonstrated. In this connection, work on the preparation of crystals of linear polysaccharides is of great importance; these polysaccharides include amyloses [160,161], inulin, mannan [162-164], xylan [164-167], and in particular cellulose [167]. Plane orthorhombic crystals of cellulose have been obtained by the slow saponification of low-molecular acetylcellulose in a dilute solution of alkali.

X-Ray and electron diffraction studies on these crystals have shown that they consist of a system of parallel plates in which the macromolecules are arranged perpendicular to the plane of the plate. The thickness of the plate varies over a range of 100 Å, i.e. it is much smaller than the length of the cellulose molecule from which the crystal is formed. It has been shown that amylose has a similar laminar-crystalline structure [160]. This phenomenon, which is characteristic of many crystallisable high polymers of linear structure [169-172], is also encountered in cellulose [167,168]. This crystalline structure of linear polymers can be explained if it is assumed that at the edge of the crystal the polymer chain turns through an angle of 180° to re-enter the lattice. Thus, the crystals described above are formed by the folding of long macromolecules in a plane perpendicular to the plane of the plate.

Manely has now obtained acetylcellulose crystals of similar structure [168-173]. When these crystals were saponified in an aqueous medium, cellulose that had a polycrystalline structure with folded macromolecules was obtained [174].

X-Ray diffraction studies on Ranby's cellulose crystals showed the presence of interferences in the same positions and of the same intensity as those found with highly oriented hydrocellulose fibres (cellulose II); no new interferences were noted (Fig. 4).

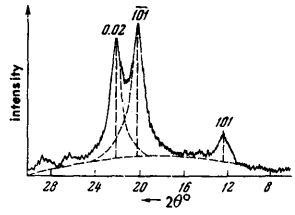


Fig. 4. X-Ray diffraction pattern of crystalline cellulose II powder.[167]

It is interesting that up to 50–60% of all the hydroxy--groups in these crystals are readily exchanged for deuterium in heavy water, that is, they behave in the same way as the groups in ordinary cellulose. Like ordinary hydrocellulose fibres and films, cellulose crystals obtained at a temperature of 30–90° form cellulose II, but those obtained at 120–150° form cellulose IV. The paper by Wolfrom and Dacons[113] mentioned above also provides evidence for the existence of cellulose crystals; these workers showed that, in the crystalline state, the products of the partial hydrolysis of cellulose — from cellotetraose to celloheptaose — gave X-ray diffraction patterns typical for cellulose II.

Whistler made a similar observation for linear xylan molecules[175], the only difference being that here the lowest compound to give a pattern similar to that of crystalline xylan was the hexasaccharide.

These examples show that crystalline formations in cellulose II give X-ray diffraction patterns similar to the patterns for oriented regenerated cellulose. If these formations are regarded as polymer (cellulose) crystals — and there are sufficient grounds for this assumption — we must recognise that similar crystalline structures are present in fibres and films of regenerated cellulose. Obviously, this conclusion can also be extended to natural fibres.

Since macromolecules with a folded structure were found to occur in the interior of various polymers of a crystalline nature, it must be assumed that similar formations can occur also in the interior of regenerated cellulose. It is assumed that in natural microfibrils the macromolecules are arranged longitudinally, but in the microfibrils of regenerated cellulose folded and unfolded macromolecules are present in various proportions.

How the packets or crystalline formations made up of folded macromolecules form sufficiently strong fibres is still obscure. It has been suggested that one end of some macromolecules enters one packet while the other end enters another packet, and in this way a mutual bond is formed along the fibre[172].

In contrast to this view, some workers regard the microfibrils as tubes formed from a solid band folded spirally in which the cellulose macromolecules are arranged perpendicular to the axis of the band in the folded state, as in crystals[160]. It should, however, be noted that these hypotheses need to be critically evaluated.

On the basis of the experimental work cited here, natural and highly oriented regenerated cellulose can be regarded as linear polymers made up of alternate highly oriented and poorly oriented sections. The highly oriented sections are similar in structure to the crystalline formations characteristic of a number of linear polymers.

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MACROKINETICS OF CHEMICAL PROCESSES

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I. INTRODUCTION

A characteristic feature of modern chemical processes, occurring at high rates at high temperatures and pressures in multiphase systems, is their great complexity. This complexity is shown in the large number and wide variety of the parameters determining the course of the processes and the large number of internal relations between the parameters and their mutual influence, the change in one parameter entailing a non-linear change in others. The complexity is enhanced by the occurrence of feedback between the parameters and also by the development of competing modes of the process, whereby the course of the latter is altered.

The complexity of a chemical process makes it necessary to understand it in terms of *models*, i.e. systems which reflect the individual aspects of the phenomena in a given process, restricted to the required conditions. Models are represented in terms of a definite mathematical notation, which establishes the relation between the parameters of the process, using both theoretical methods and experimental data. In their analysis and use, such models are usually divided into separate blocks, purely chemical phenomena, determined by classical chemical kinetics, being considered separately; blocks taking into account mass and energy transfer during the chemical reaction are distinguished. In this connection it has become usual to distinguish the micro- and macro-kinetics of chemical processes. This subdivision is of course to a certain extent arbitrary, but it makes

possible an accurate quantitative estimate of various aspects of a complex chemical process, so that it constitutes, in consequence, the scientific basis of industrial chemical processes.

The modern concept of macrokinetics was introduced by Frank-Kamenetskii [1], who also indicated the problems and the scope of this concept. Subsequently macrokinetics were formulated as a special branch of chemical kinetics and became the basis for the calculation of the parameters of chemical reactors and industrial chemical processes. Ten years after the appearance of Frank-Kamenetskii's paper, a special Symposium of the European Federation of Chemical Engineers devoted to the problems of macrokinetics was held in Amsterdam in 1957. [2] With the advent of computer techniques, the macrokinetics of chemical processes have entered a new stage of development — there is now a possibility of mathematically modelling chemical processes, their optimisation, and control [3-5]. The problems of macrokinetics have been further considered in Levich's papers [6].

Microkinetics deal with reactions in a chemical process at the molecular level on a scale not exceeding the mean free path of the molecules. Molecular friction (viscosity), molecular heat transport (thermal conductivity), and molecular matter transport (molecular diffusion) are also included among phenomena on the scale of molecular interactions.

In the study of processes at two levels, the state of liquid media becomes important. The mixing of liquids is called microscopic if it is restricted to the mixing of individual molecules; such a state of the liquid is called a micro-state [7,8]. Classical chemical kinetics are based on kinetic equations corresponding to micro-states.

Macrokinetics are concerned with the study of the interactions in a chemical process at the level of molecular aggregates on the scale of eddies, drops, or gas bubbles, i.e. on the scale of the so-called macro-particles. The mixing of liquids is regarded as macroscopic if it occurs on interaction between macro-particles. Consequently such a liquid state is referred to as macroscopic.

Examination of macro- and micro-mixing is important for heterogeneous systems, since one of the phases in such systems usually behaves as a liquid in a macro-state. For example, the solid phase in liquid–solid systems may be interpreted as a liquid in a macro-state, since each species of the solid constitutes a definite molecular aggregate. The disperse phase in liquid–liquid systems may serve as another example. Segregation in such systems increases with the surface tension.

Homogeneous systems behave as liquids in a micro-state, except for very viscous liquids or systems in which very rapid reactions take place. In the latter two cases the time required for the homogenisation of the system may prove to be appreciable compared with the rate of reaction and therefore the latter is limited by the mixing process.

The principal problem in macrokinetics is to establish the laws governing the transport of matter and energy on the macroscopic level under real conditions of chemical processes. The problem reduces to determining the distribution of concentrations and temperatures in the reactor as a function of the organisation of the reactant streams, heat inflow or outflow, and the effect of diffusion. For example, in contact-catalytic processes in a stationary catalyst bed one examines on the macroscopic level the distribution of temperatures and concentrations in the radial and axial directions in the bed under the usual non-isothermal and non-adiabatic conditions. On the microscopic level under these conditions, one examines the distribution of heat and concentrations within the catalyst particle (and within its pores).

Evidently, in the examination of a chemical process as a whole micro- and macro-kinetics constitute a single unity. However, this does not mean that the problems involved in the study of macrokinetics cannot be of independent interest, by virtue of the specificity of the scale of the objects examined and the specificity of the laws which obtain on macroscopic levels.

Accordingly, the study of chemical processes in industrial reactors comprises two aspects. Under laboratory conditions, the microkinetics of the process are investigated, whereby the reaction mechanism is established and the kinetic equations are derived. Using an experimental reactor of the chosen design, the parameters of the models which determine the macrokinetics of the process are established — the coefficients of longitudinal and radial mixing, the flow conditions, the coefficients of mass and heat transfer, etc. are determined. The micro- and macro-kinetic parameters are then combined into a complete mathematical model from which graphical and numerical relations between all the process parameters may be obtained by the method of mathematical modelling (the principle is that the deformation of the model is not studied using an actual physical model, as in physical modelling, but directly on the mathematical model itself using electronic computers) and the optimum conditions may be found (using the familiar optimisation methods). Thus the study of macrokinetics constitutes the basis of the modern analysis of industrial chemical processes. The mathematical models of chemical processes, taking into account the phenomena of energy and mass transport, which are superimposed on purely chemical phenomena in order to emphasise the importance of and necessity for the study of the problems of the macrokinetics of chemical processes, are examined below.

II. MATHEMATICAL MODELS OF ISOTHERMAL IDEAL REACTORS

It has become customary to examine the operation of real reactors by comparing them with ideal models. Usually the analysis is based on two extreme models: the ideal plug flow model and the ideal backmix flow model. The possibility of choosing such models was first pointed out by Kirillov [9], who gave a quantitative treatment of the elutriation phenomenon. Quantitative estimates of the course of chemical processes in the above models have been made [10,11].

The ideal plug flow model corresponds to the state in which the components are continuously introduced into the reactor and removed from it (Fig. 1); longitudinal and transverse mixing of the medium particles is then completely absent. The residence time of all the particles in the reactor is the same and equal to the ratio of the volume of the reactor to the volume flow rate of the liquid. The composition of the liquid and the reaction rate vary from point to point along the length of the reactor. The relation between the residence time in the reactor and the rate of reaction is established on the basis of the material balance of the reactor.

The following notation will be used: V_A is the influx of reactant A in kmole s^{-1}, V_r the reaction volume in litres, x_A the conversion defined as $x_A = (c_{A_0} - c_A)/c_{A_0}$, c_{A_0} and

c_A are the initial and final concentrations of reactant A in kmole litre^{-1}, and w_{r_A} is the rate of reaction (the rate of conversion of reactant A) in kmole s^{-1}.

For a steady stream and a constant reactor cross-section, one can write, in accordance with Fig. 1,

$$V_A - (V_A + dV_A) + (-w_{r_A})dV_r = 0 \qquad (3)\dagger$$

whence

$$-dV_A + (-w_{r_A})dV_r = 0.$$

Bearing in mind that $V_A = V_{A_0}(1 - x_A)$ and $dV_A = -V_{A_0}dx_A$, we obtain after substitution in Eqn. (3), separation of variables, and integration:

$$\frac{V_r}{V_{A_0}} = \int_0^{x_A} \frac{dx_A}{w_{r_A}}. \qquad (4)$$

On introducing the concentration c_{A_0}, defined as the number of kilomoles per unit volume and the volume per second V_s (in litre s^{-1}), one can write

$$V_{A_0} = c_{A_0}V_s. \qquad (5)$$

Evidently the ratio V_r/V_s, which has the dimensions of time, is the residence time τ_n of the reactant in the reactor, and therefore one can write

$$\tau_n = \frac{V_r}{V_s} = c_{A_0}\int_0^{x_A} \frac{dx_A}{w_{r_A}} \text{ (seconds)}. \qquad (6)$$

In the general case for a reaction of an arbitrary nth order the rate of reaction w_{r_A} can be written thus:

$$-w_{r_A} = kc_A^n = kc_{A_0}^n(1-x_A)^n. \qquad (7)$$

After substitution of Eqn. (7) in Eqn. (6), we obtain

$$\tau_n = \frac{V_r}{V_s} = c_{A_0}\int_0^{x_A} \frac{dx_A}{kc_A^n} = \frac{1}{k}c_{A_0}^{1-n}\int_0^{x_A} \frac{dx_A}{(1-x_A)^n} \text{ (seconds)}. \qquad (8)$$

Tubular reactors with a large tube length : diameter ratio (longitudinal mixing may be neglected) with a turbulent flow of liquid or gas (radial mixing may be neglected in view of the planar velocity profile in turbulent motion) are based on the ideal plug flow model. The plug flow model also fits a periodic reactor, but with respect to the time coordinate and not the length coordinate.

The ideal backmix flow model corresponds to the state in which it is assumed that the components are continuously introduced into and removed from the reactor (at the same rate); the mixing of the medium particles in the reactor is so complete that the concentration of each component is the same throughout the volume.

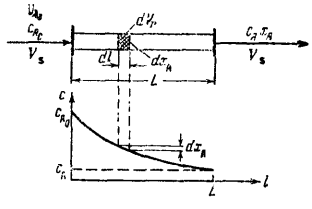


Fig. 1. The structure of the ideal plug flow reactor model.

According to the material balance equation for this model, we have

$$V_s(c_{A_0} - c_A) = (-w_{r_A})V_r. \qquad (9)$$

By analogy with Eqn. (6), the residence time of the reactant in the reactor τ_n' can be represented by the expression

$$\tau_n' = \frac{V_r}{V_s} = \frac{c_{A_0} - c_A}{(-w_{r_A})} = \frac{c_{A_0} - c_A}{kc_A^n} = \frac{1}{k}c_{A_0}^{1-n}\frac{x_A}{(1-x_A)^n}. \qquad (10)$$

Comparison of the conversions in ideal plug flow and ideal backmix flow models of the reactor for the same residence time and a first-order reaction with $k = 1$ yields the curves in Fig. 2. It follows from the graph that in an ideal backmix flow reactor the conversion x_A is lower than in an ideal plug flow reactor. Thus a conversion of 0.85 in an ideal plug flow reactor can be attained in 19 min while in an ideal backmix flow reactor the time required is 57 min.

We may note that, when the reaction medium passes through the plug flow reactor, the conversion increases along the length of the reactor and, since for simple reactions the rate decreases with conversion, the average rate is between the maximum value at the inlet to the reactor and the minimum value at the outlet. When the reaction medium passes through the backmix flow reactor, the conversion at each point in the reactor corresponds to the conversion at the outlet and the average rate is equal to the low value at the outlet from the reactor. Consequently, when the two reactor models are compared under isothermal conditions for the same conversion at the outlet, the average reaction rate in the plug flow reactor is always higher and therefore the required volume of a reactor of this type is smaller.

The model of the reactor affects not only the conversion but also the distribution of the reaction products. We shall examine as an example the decomposition of a component A which can occur in two ways [12]:

$$a_1A \xrightarrow{k_1} R \text{ (desired product)}$$
$$a_2A \xrightarrow{k_2} S \text{ (undesired product)}$$

at rates defined by Eqns. (11) and (12):

$$w_{r_R} = \frac{dc_R}{d\tau} = k_1c_A^{a_1} \qquad (11)$$

$$w_{r_S} = \frac{dc_S}{d\tau} = k_2c_A^{a_2}. \qquad (12)$$

On dividing Eqn. (12) by Eqn. (11), we obtain the ratio of the rates of formation of products S and R:

$$\frac{w_{r_S}}{w_{r_R}} = \frac{k_2}{k_1}c_A^{a_2-a_1}. \qquad (13)$$

It follows from Eqn. (13) that only by varying the concentration c_A is it possible to change the product concentration ratio c_S/c_R, since the kinetic parameters k_1, k_2, a_2, and a_1 are constant for a given system at a given temperature.

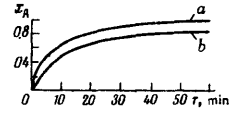


Fig. 2. Conversion in ideal plug flow (curve a) and ideal backmix flow (curve b) models.

† Eqns. (1) and (2) are missing in the Russian original (Ed. of Translation).

Their influence on the distribution of products is shown as follows.

1. If $a_1 > a_2$, i.e. the reaction order for the desired product is higher than the reaction order for the undesired product, then $a_2 - a_1$ is negative. According to Eqn. (13), to obtain relatively high yields of the desired product R, it is necessary to have a high concentration of the reactant A (c_A) in the reactor, which can be achieved in one of the following ways: (a) by using an ideal plug flow reactor, where the concentration c_A decreases gradually from initial high values; (b) by increasing the total pressure in gas-phase systems or by eliminating inert impurities, whereby the concentration of the reactant at the inlet to the reactor is increased; (c) by eliminating the product recycle flow.

2. If $a_1 < a_2$, i.e. the reaction order for the desired product is lower than for the undesired product, the preferential formation of the product R requires lower concentrations of the reactant, which is achieved by one of the following procedures: (a) by using an ideal backmix flow reactor in which the concentration of the reactant rapidly attains the minimum value corresponding to the outlet; (b) by introducing a recycle flow, whereby the inlet concentration and the concentration of reactant A in the reactor are reduced; (c) by reducing the pressure or increasing the concentration of inert gases in gas-phase systems. All these measures necessitate a large reactor. In this case the optimum design is achieved by comparing the economic balance of the cost of removal of the undesired product and the large capital outlay required for larger plant.

3. If $a_1 = a_2$, i.e. both reactions are of the same order, Eqn. (13) becomes

$$\frac{w_{r_S}}{w_{r_R}} = \frac{dc_S}{dc_R} = \frac{k_2}{k_1} = \text{const} \qquad (14)$$

i.e. the distribution of products is constant for a given rate constant ratio k_2/k_1 and independent of the type of reactor. The ratio of the products may be varied by changing the ratio k_2/k_1 in the following way: (a) by changing the temperature conditions of the process, when the activation energies for the two reactions differ from one another; (b) by using a selective catalyst.

Fig. 3 shows the variation of the relative yield of the intermediate product R with the kinetic parameters and the type of reactor [12] for the consecutive reaction

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S.$$

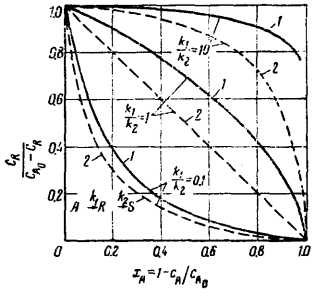


Fig. 3. Relative yield of the intermediate product in ideal plug flow (curve 1) and ideal backmix flow (curve 2) reactors for various conversions of the starting material.

On the basis of Fig. 3, we may conclude firstly, that the yield of the intermediate product R in the plug flow reactor is always higher than in the backmix flow reactor, and, secondly, that for high k_1/k_2 ratios the conversion is high, and vice versa for low ratios, i.e. under these conditions recycle flow should and should not be used respectively.

The distribution functions for the products of parallel consecutive reactions can be very conveniently and rapidly analysed by analogue computers. Structured assembly schemes have been proposed for the solution of problems of this kind by analogue computer; typical chemical reactions have been examined and the optimum yields of products have been calculated [13].

III. MATHEMATICAL MODELS OF ISOTHERMAL NON-IDEAL REACTORS

1. General Postulates

In contrast to the ideal reactors examined above, in non-ideal reactors the distribution of the reacting particles of the medium along the stream and along the stream cross-section is non-uniform. For this reason, in such reactors account must be taken of the transverse and longitudinal mixing of the medium particles. The distribution function of concentrations with respect to time is used as one of the characteristics in the operation of non-ideal reactors. A second characteristic is the state of segregation of the particles, i.e. a distinction must be drawn between processes at a micromixing level (at a molecular level) and processes at a macromixing level (the level of molecular aggregates). The level corresponding to the state of the system is defined by the so-called degree of separation of the system or the degree of segregation I introduced by Danckwerts [7]. The concepts of the "concentration at a point" and the "age of the liquid at a point" are introduced in connection with the concept of the degree of segregation. They denote the concentration, or age, averaged over a very small space compared not only with the system as a whole but also compared with the dimensions of the molecular aggregates and yet large enough to contain many molecules.

If the age of a molecule is defined as the time τ elapsed from the instant when the molecule entered the system, the variance of the age of all the molecules of the system, i.e. the average square of the deviations of the molecular ages from the average age, may be calculated:

$$\text{Var}\,\tau = \overline{(\tau - \bar{\tau})^2}, \qquad (15)$$

where $\bar{\tau}$ is the average age of all the molecules present in the system at a given instant; the overall bar over the symbols denotes an average value for all the molecules.

If the average molecular age at each "point" is denoted by τ_p, the variance of the age may serve as a measure of the degree of separation. The variance is

$$\text{Var}\,\tau_p = \overline{(\tau_p - \bar{\tau})^2}, \qquad (16)$$

where the overall bar denotes averaging over all the points.

If mixing takes place at a molecular level, the average age of all the molecules at each point is the same and equal to the average in the system and the variance of the age at different points is then zero.

If mixing takes place at a macroscopic level, i.e. the system is completely separated (segregated), the variance

of the age at different points in the system is equal to the variance of the age of all the molecules, i.e.

$$I = \frac{\mathrm{Var}\,\tau_p}{\mathrm{Var}\,\tau} = 1. \qquad (17)$$

For any other degree of separation, I will be less than unity:

$$I = \frac{\mathrm{Var}\,\tau_p}{\mathrm{Var}\,\tau}\,\frac{\overline{(\tau_p - \bar{\tau})^2}}{(\tau - \bar{\tau})^2} < 1. \qquad (18)$$

The limiting value $I = 0$ corresponds to the state of maximum mixedness, a concept introduced by Zwietering[8].

For a system in which the distribution of residence times is equal to the distribution in an ideal backmix flow model, I may be between zero (mixing at a molecular level) and unity (complete segregation). In a system corresponding to the ideal plug flow model, where there is no mixing of the stream particles, the degree of separation attains the maximum value $I = 1$.

We shall determine the effect of the level of mixing, or the state of the system, on the conversion in the reactors. Consider two arrangements of two reactors corresponding to two extreme models: the ideal plug flow and ideal backmix flow models connected in series (Fig. 4). The difference between the two schemes consists in the fact that in scheme *a* mixing takes place at a later stage and in scheme *b* at an earlier stage. The overall distribution of residence times in both reactor arrangements will be the same — the usual delta-function (see below) is obtained for the plug flow zone and an exponential function for the backmix flow zone.

If these two systems are regarded solely as different types of flow apparatus without chemical reaction, designed, for example, to lower the temperature and concentration variation in a steady stream of liquid, their effects will be completely the same. The difficulty in the study of chemical reactors arises from the fact that usually the mixing of the elements of the liquid takes place at the same time as the chemical reaction. Although the overall mixing in both systems is the same, the mixing in the second scheme takes place at an earlier stage of the chemical reaction, while in the first scheme the mixing occurs at a later stage. This, of course, leads to different yields of the products in the systems. If the reaction is isothermal and of an order greater than unity, a higher conversion will be attained in the first arrangement of apparatus. According to what has been said above, the plug flow reactor *1* corresponds to a higher degree of segregation than the backmix flow reactor *2* ($I_1 > I_2$).

On the basis of these considerations a different treatment of the effect of the level of mixing is also possible. Imagine a reactor with complete segregation, consisting of a long tube in which there is a piston-type stream or ideal plug flow, with a large number of closely packed lateral outlets (Fig. 5*a*). The stream flowing through these lateral outlets is controlled in such a way that the total distribution of residence times in the system is equal to the given distribution which is being investigated. It is assumed that the volume of the lateral outlets is insignificant. A very short section along the length of the tube may be regarded as a point in this system. Clearly the distribution of the ages at each point is extremely narrow and there is no mixing in the system, except for the mixing in the common outlet. Thus the mixing of molecules with different ages is achieved as late as possible, i.e. at point *A* (Fig. 5*a*).

A second imaginary flow system, with maximum mixing, can be obtained, by simple flow reversal, from the first flow system which is completely segregated. We then have many inlets and one outlet (Fig. 5*b*). It is assumed that mixing in the radial direction is ideal and that the flowing liquid is scattered immediately throughout the length of the tube. As soon as it enters the system, each molecule mixes with other molecules which will leave the system simultaneously. Thus mixing of the molecules occurs as soon as possible. This state is defined as the state of "maximum mixedness" — it is the opposite of the concept of total segregation[8].

Summarising the above findings, we arrive at the following most important conclusion: for a complete analysis of the operation of a chemical reactor, it is necessary to know (1) the reaction kinetics, (2) the response function of the system or the residence time distribution curve, (3) the properties of the system, i.e. the presence of macro- and micro-systems, and (4) whether mixing takes place during early or late stages.

In terms of classical kinetics, chemical reactions are considered at a microscopic level and consequently systems to which such kinetics are applied are microsystems.

The following conclusions may be made on the basis of the work of Danckwerts[7] and Zwietering[8]: (1) allowance for the degree of segregation and maximum mixedness is important only in homogeneous systems, since heterogeneous systems are always completely segregated, i.e. are always in a macrostate; (2) the degree of segregation and maximum mixedness must be taken into account only in stirred-flow tank reactors, since the streams in reactors operating on the total plug flow principle are always completely segregated; (3) in first-order reactions in homogeneous systems in stirred-flow tank reactors the conversion is independent of the level of mixing; the reaction rate is higher for the completely segregated state in reactions of an order greater than unity and lower in reactions of an order smaller than unity; (4) a plug flow reactor always

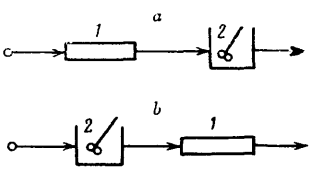


Fig. 4. Effect of the positioning of reactor models on the mixing level:
1) ideal plug flow; 2) ideal backmix flow.

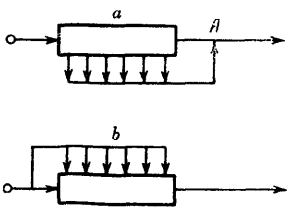


Fig. 5. Mixing in later (*a*) and earlier (*b*) stages.

gives a higher conversion than backmix flow reactors, both at the level of minimum and maximum segregation.

As mentioned above, to estimate the degree of non-uniformity of the distribution of the medium particles and hence the concentrations of the reactants in reactors, the corresponding distribution function is found by a statistical treatment of the experimental data on the variation of the concentration at the outlet from the reactor as a result of perturbations at the inlet, i.e. a cybernetic method is used to analyse the transmission of the signal through the test object.

Usually in the analysis of the distribution function for concentrations in reactors three types of perturbation (or, correspondingly, three types of input signal), differing in the mode of introduction of the tracer at the inlet, are used: step perturbation (step signal), pulse input signal (delta-function), and sinusoidal perturbation (frequency response) (Fig. 6).

At the outlet from the reactor the corresponding output signal (the time variation of tracer concentration at the outlet), whose form depends on the hydrodynamic conditions of the streams in the reactor, is obtained. The time parameter can be conveniently represented in the dimensionless form $\theta = \tau/\overline{\tau} = V_s\tau/V_r$, where τ is time in general and $\overline{\tau}$ the residence time of the tracer in the reactor, equal to the ratio of the volume of the reactor V_r filled with liquid to the volume of liquid V_s flowing in 1 s.

Step perturbation — *F* curve. In step perturbation the concentration of the tracer at the inlet reaches abruptly a constant value c_0. The distribution of the concentrations c at the inlet is then obtained in the form of the so-called *F*-curve, ranging from zero to $c/c_0 = 1$ (Fig. 6*a*).

Delta-function — *C* curve. In the case of pulse tracer injection (delta-function) the so-called *C* curve, shown in Fig. 6*b*, is obtained at the outlet.

Sinusoidal perturbation (frequency response). When the rate of injection of the tracer is varied harmonically, a sinusoidal curve, with a modified amplitude and phase angle, is obtained at the outlet (Fig. 6*c*).

The statistical distribution function for the tracer in the case of pulse perturbation can be written in the form (*C* curve)

$$C = \int_0^\infty \tau C(\tau)\, d\tau. \qquad (19)$$

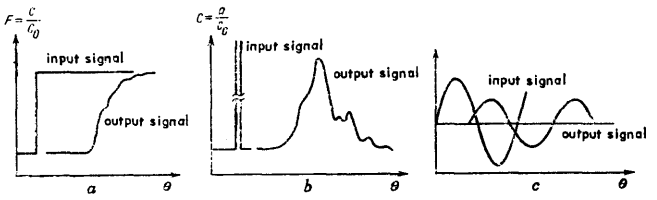


Fig. 6. The types of perturbation (input and output signals) used in the determination of the type of reactor model:
a) stepwise perturbation (*F* curve); *b*) delta-function (*C* curve);
c) frequency-response curves.

The residence time distribution function $C(\tau)$ characterises the fraction of the substance (tracer) in the exit stream which remained in the system for a time smaller than τ. The average residence time $\overline{\tau}$ is determined from the relation

$$\overline{\tau} = \frac{\int_0^\infty \tau C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \simeq \frac{\Sigma \tau c}{\Sigma c}. \qquad (20)$$

The distribution function $C(\tau)$ is put in the form

$$C(\tau) = \frac{1}{\tau}\frac{c}{c_0} = \frac{c_0}{\Sigma c\, \Delta\tau}\ (s^{-1}), \qquad (21)$$

where $\Delta\tau$ is the sampling interval.

The dimensionless residence time θ is

$$\theta = \frac{\tau}{\overline{\tau}}.$$

When the average residence time is known, the *C* curve may be characterised by the equation

$$C = \frac{c}{c_0} = \overline{\tau} C(\tau). \qquad (22)$$

The variance or scatter of the quantity under consideration about the mean (for a continuous distribution), for a finite number of equidistant points (equal sampling intervals), is defined by the formula

$$\sigma^2 = \frac{\Sigma x_i^2 f(x_i)}{\Sigma f(x_i)} - \left[\frac{\Sigma x_i f x_i}{\Sigma f(x_i)}\right]^2. \qquad (23)$$

Thus when the variance is expressed in units of time, i.e. σ_τ^2 has the dimensions $(\text{seconds})^2$, we have

$$\Sigma f(x_i) = \Sigma c_i;\ \Sigma x_i f(x_i) = \Sigma \tau_i c_i;\ \Sigma x_i^2 f(x_i) = \Sigma \tau_i^2 c_i;$$
$$\sigma_\tau^2 = \Sigma \tau^2 C(\tau)\Delta\tau - (\overline{\tau})^2.$$

The following expression holds for the variance in dimensionless units:

$$\sigma^2 = \frac{\sigma_\tau^2}{(\overline{\tau})^2} \qquad (23a)$$

or for the *C* distribution of the dimensionless time θ we have

$$\sigma^2 = \frac{\Sigma \theta^2 C}{\Sigma C} - 1 = \Sigma \theta^2 C \Delta\theta - 1. \qquad (23b)$$

The relation between the distribution functions for step and pulse perturbation is given by

$$C = \frac{dF}{d\theta};\quad F = \int_0^\theta C\, d\theta.$$

Since $C(\tau)d\tau$ characterises the fraction of the substance in the exit stream with the ages τ and $\tau + d\tau$, on multiplying this quantity by the concentration c_A of the reactant remaining in the element of stream with the age $\tau + d\tau$, we can determine the average concentration $\overline{c}_A$ of the unreacted reactant leaving a real reactor:

$$\overline{c}_A = \int_{\tau=0}^{\tau=\infty} c_A C(\tau)\, d\tau. \qquad (24)$$

Eqn. (24) is valid only for linear processes in which the output signal is directly proportional to the input signal and which therefore have the property of additivity. Bearing in mind that for first-order reactions the concentrations are related by the expression

$$c_A = c_{A_0} e^{-k\tau}$$

we can write, in conformity with Eqn. (24),

$$\bar{c}_A = c_{A_0} \int_0^\infty e^{-k\tau} C(\tau)\, d\tau. \qquad (25)$$

Thus if information is available about the kinetics of the chemical reaction, we can determine by Eqn. (25) the conversion in a non-ideal reactor from the distribution curve $C(\tau)$ obtained experimentally for the given type of reactor.

Frequency response. The frequency response is obtained when the variation of the amount of tracer added is periodic (Fig. 6) at a definite frequency; the variation of tracer concentration at the inlet and outlet is then characterised by sinusoidal curves mutually displaced in amplitude and phase. The use of the method of frequency response for the analysis of reactors has been described by Kramers and Alberda [14] and has been developed by Mayer and Rippel [15]. Frequency analysis permits the replacement of time functions with the aid of the Laplace operator method. The Laplace operator is defined by the expression

$$F(p) = \int_0^\infty e^{-p\tau} f(\tau)\, d\tau. \qquad (26)$$

In this method the time function $f(\tau)$ describing the behaviour of the reactor is replaced by the so-called transfer function $F(p)$. The latter is the ratio of the output function $F_{outp}(p)$ transformed by the Laplace method to the Laplace input function $F_{inp}(p)$:

$$F(p) = \frac{F_{outp}(p)}{F_{inp}(p)}. \qquad (27)$$

If the transfer function is set up over a wide range of frequencies, it is possible to obtain a frequency response diagram which is then compared with the known frequency response diagram for ideal reactor models. Table 1 presents typical transfer functions for ideal reaction models and first-order reactions. By combining different models, it is possible to estimate the transfer function for a real reactor.

Consider an ideal backmix flow reactor in which a first-order reaction takes place. The following notation is introduced: V_s is the space velocity, c_{inp} the concentration of the reactant at the inlet, c_{outp} the concentration of the reactant at the outlet, k the reaction rate constant, and V_r the volume of the reactor. The material balance equation can be written in the form

$$V_s c_{inp} - V_s c_{outp} - k c_{outp} V_r = V_r \frac{dc_{outp}}{d\tau}. \qquad (28)$$

After Laplace transformation, we have the equation

$$V_s c_{inp}(p) - V_s c_{outp}(p) - k c_{outp}(p) V_r = V_r c_{outp}(p)\, p, \qquad (29)$$

where p is a Laplace operator.

The following expression for the concentrations of the reactant at the inlet to, and outlet from, the reactor can be obtained from Eqn. (29):

$$\frac{c_{outp}(p)}{c_{inp}(p)} = \frac{\frac{V_s}{V_r}}{\left(\frac{V_s}{V_r} + k + p\right)}. \qquad (30)$$

On introducing the time constant $V_r/V_s = T$, we obtain the equation

$$\frac{c_{outp}(p)}{c_{inp}(p)} = \frac{1}{T\left(\frac{1}{T} + k + p\right)} \qquad (31)$$

or

$$\frac{c_{outp}(p)}{c_{inp}(p)} \frac{1}{Tp + Tk + 1}. \qquad (32)$$

The relation obtained describes a state which varies with time, i.e. a non-steady state. Since usually c_{outp}/c_{inp} is measured in the steady state where p is close to zero, Eqn. (32) can be reduced to the form

$$\frac{c_{outp}(0)}{c_{inp}(0)} = \frac{1}{Tk + 1}. \qquad (33)$$

When Eqn. (33) is compared with the transfer function for the total backmix flow reactor (see Table 1), it is seen that the equation for first-order reaction kinetics in the steady state can be obtained from the transfer function on replacing p by the rate constant k. This opens up the possibility of assessing the process kinetics from the frequency response.

Two models based on the ideal reactor concept are used to analyse the operation of real reactors with non-linear systems. These models are the plug flow model with longitudinal or radial mixing (dispersion model) and the model with total mixing in individual tanks joined together in series, but without mixing of the contents of the different tanks (the tanks-in-series model).

TABLE 1. Typical transfer functions for ideal reactor models with first-order reactions.

Type of reactor	Transfer function	Remarks
Ideal backmix flow	$\frac{1}{T_1 p + 1}$	$T_1 = V_r/V_s$; V_r is the reactor volume and V_s the space velocity of the liquid
Ideal plug flow	e^{-pT_d}	$T_d = L/w$ is the transport lag, L the reactor length, and w the linear flow rate of the liquid
N ideal backmix flow reactors of equal volume in series (staged reactors)	$\frac{1}{(T_1 p + 1)^n}$;	
N ideal backmix flow reactors of unequal volume in series	$\frac{1}{(T_1 p + 1)(T_2 p + 1) \ldots (T_n p + 1)}$;	$T_1 = V_{r_1}/V_s$ $T_n = V_{r_n}/V_s$
Ideal plug flow and ideal backmix flow reactors in series	$\frac{e^{-pT_d}}{T_1 p + 1}$	

2. The Dispersion Model

As stated above, this model is based on the plug flow model with longitudinal and radial mixing. The coefficient of longitudinal or radial mixing D_L is analogous to the molecular diffusion coefficient in Fick's diffusion equation:

$$\frac{\partial c}{\partial \tau} = D_L \frac{\partial^2 c}{\partial l^2}. \qquad (34)$$

In the theory of mass transport [16] the coefficient D_L is also called the coefficient of turbulent diffusion or of eddy transport, which describes its physical nature. For this reason, the model can also be called the *eddy model*.

The equation for the transport of the substance at a macroscopic level in a steady stream with allowance for

longitudinal mixing and chemical reaction takes the following form on the basis of the law of the conservation of matter:

$$w\frac{dc_A}{dl}-D_L\frac{\partial^2 C_A}{\partial l^2}+kc_A^n=0. \quad (35)$$

Eqn. (35) is normally used in a dimensionless form. For this purpose, we put $z = l/L$ and $\tau = L/w = V_r/V_s$, where L is the length of the reactor, w the linear flow rate across the total cross-section, V_r the reactor volume, and V_s the space velocity of the stream. On multiplying all the terms of Eqn. (35) by τ, we obtain

$$\frac{dc_A}{dz}=\frac{D_L}{wL}\frac{\partial^2 c_A}{\partial z^2}+k\tau c_A^n=0. \quad (36)$$

Introducing the conversion $x_A = (c_{A_0} - c_A)/c_{A_0}$, we obtain

$$-\frac{dx_A}{dz}+\frac{D_L}{wL}\frac{\partial^2 x_A}{\partial z^2}+k\tau c_{A_0}^{n-1}(1-x_A)^n=0. \quad (37)$$

In order to solve the above equation, it is necessary to know the value of the coefficient D_L, which is determined independently or from the experimental concentration distribution curve with respect to time, considered above for homogeneous and heterogeneous systems.

Usually the coefficient of longitudinal or radial mixing is determined in the dimensionless form D_L/wL, as in Eqn. (37), which is the reciprocal of the Peclet number $Pe = wL/D_L$. The choice of the linear dimension L, which is the determining dimension, is important. The dimensionless parameter D_L/wL varies from zero for an ideal plug flow stream to 1 for a total backmix flow stream.

Homogeneous systems. The distribution curves examined above, together with the values of the parameter D_L/wL, make it possible to determine the real reactor model, however much it may differ from ideal reactor models.

Fig. 7 shows C and F curves for a closed vessel corresponding to different values of the dimensionless parameter D_L/wL, in which the determining dimension L has been assumed to be the distance from the stream inlet to the stream outlet in the closed vessel. Levenspiel and Smith [17] and also Van der Laan [18] found from the C curve the relations between the variance σ^2 and the dimensionless parameter D_L/wL. For low deviations from ideal plug flow, which often obtain in tubular reactors, the C curves approximate closely to the normal Gaussian distribution and the relation between the variance and D_L/wL is represented by the equation

$$\sigma^2 = 2\frac{D_L}{wL}. \quad (38)$$

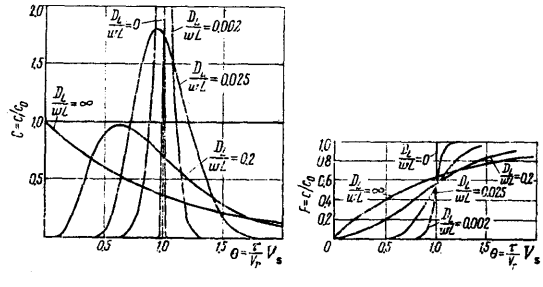


Fig. 7. Variation of output curves (C and F) with D_L/wL and θ.

When $D_L/wL < 0.01$, the maximum error associated with the use of Eqn. (38) is less than $5(D_L/wL)$, i.e. 5% when $D_L/wL = 0.01$ or 0.5% when $D_L/wL = 0.001$.

Table 2 presents different ways of using the dispersion models in homogeneous reactions under isothermal conditions [19].

Heterogeneous systems. In view of the importance of heterogeneous gas–solid systems for the analysis and calculation of the parameters of contact-catalytic processes, a large number of studies have been made [14,34-40] on the quantitative relation between the Peclet number for longitudinal ($Pe_L = d_p w/D_L$) and radial ($Pe_R = d_p w/D_R$) mixing and the Reynolds number Re in such systems. The particle diameter d_p is used as the determining dimension in the Peclet and Reynolds numbers, and the linear velocity of the liquid (gas) w is referred to the total cross-section of the apparatus. The results of these investigations are represented schematically in Fig. 8.

Fig. 8 shows that under turbulent conditions in gases and liquids the radial number Pe_R for mass transport is close to 12 (curve A), which agrees with Baron's theoretical calculations [41]. The Peclet number for longitudinal mixing in gases is approximately 2, which is also consistent with theoretical calculations [34,41], but differs from the experimental values for liquids. At low Re numbers, the "radial" and "longitudinal" Peclet numbers deviate from 2 and 12. In this case molecular diffusion has a significant influence.

Solution of the general form of the equation for the dispersion model. Because of its non-linearity, Eqn. (37) can be solved for specified boundary conditions only by numerical methods using computers.

TABLE 2. Different modes of utilisation of dispersion models.

Reaction order	Type of reaction	Type of flow	Mode of diffusion [dispersion]	References
0		turbulent	longitudinal	7,20,21
1/6–1/3	irreversible	turbulent	longitudinal	20
1	irreversible	laminar	radial	22–27
1	irreversible	turbulent	longitudinal	21,26–31
1	irreversible	turbulent	radial	23, 24
1	consecutive	turbulent	radial	27
1	reversible	turbulent	longitudinal	32
2	irreversible	laminar	longitudinal	31
2	irreversible	laminar	radial	22, 26
3	irreversible	turbulent	longitudinal	20, 30
	irreversible	turbulent	longitudinal	33

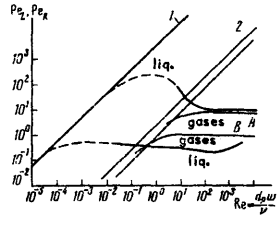


Fig. 8. Variation of the longitudinal (Pe_L) and radial (Pe_R) Peclet numbers with the Reynolds number Re:
1) molecular diffusion of liquids; 2) molecular diffusion of gases; A) radial diffusion; B) longitudinal diffusion.

The analytical solution of Eqn. (37) has been achieved only for first-order reactions. The following expression was obtained:

$$\frac{c_A}{c_{A_0}} = 1 - x_A = \frac{4a \exp\left(\frac{1}{2}\frac{wL}{D_L}\right)}{(1+a)^2 \exp\left(\frac{a}{2}\frac{wL}{D_L}\right) - (1-a)^2 \exp\left(-\frac{a}{2}\frac{wL}{D_L}\right)}, \quad (39)$$

where

$$a = \sqrt{1 + 4k\tau\left(\frac{D_L}{wL}\right)}.$$

The numerical solution of Eqn. (37) for first- and second-order reactions was achieved by Levenspiel and Bischoff[30] and by Fan and Bailie[28]. Levenspiel and Bischoff presented their solution in the form of graphs for different values of Pe_L, in which the ratio of the real reactor volume (taking into account longitudinal mixing) to the ideal plug flow reactor volume is plotted against the fraction of the unreacted reactant $c_A/c_{A_0} = 1 - x_A$. They concluded that for low conversions longitudinal mixing does not have much effect and the difference in the volumes of the ideal and real reactors is insignificant. It should be borne in mind that the dispersion model yields reliable results for comparatively small deviations from the ideal plug flow model and therefore the graphs described above can be used only for relatively low values of the parameter D_L/wL.

Effect of radial mixing. The effect of radial mixing is shown when the ratios of the tube diameter to particle diameter are low. Radial mixing is significantly influenced by the radial temperature profile, which leads to non-uniformity in conversion. A logical consequence of the radial gradient is a high rate of heat flow to and from the walls of the reactor. In principle, radial transport is an entirely desirable phenomenon for the elimination of hot spots along the reactor axis. The rate of radial diffusion may be increased by choosing a suitable ratio of tube diameter to particle diameter and a suitable temperature of the walls of the cooled reactor.

3. The Tanks-in-Series Model

The tanks-in-series model is based on the concept of the subdivision of the apparatus (reactor) into separate tanks. Within each tank ideal mixing takes place but there is no mixing between different tanks.

The relation between the C curve distribution and the number of tanks N is defined by the expression

$$C = \frac{c}{c_0} = \frac{N\theta^{N-1}}{(N-1)!} e^{-N\theta}, \quad (40)$$

where

$$\theta = \frac{\tau}{V_r/V_s}.$$

The relation between the number of tanks N and the variance σ^2 is

$$\sigma^2 = \frac{1}{N} = 2\frac{D_L}{wL} - 2\left(\frac{D_L}{wL}\right)^2\left(1 - e^{-\frac{wL}{D_L}}\right) \quad (41)$$

or Eqn. (38) can be used with adequate accuracy for practical calculations:

$$\sigma^2 = \frac{2}{N} = 2\frac{D_L}{wL}.$$

Assuming total mixing of the gas within the free volume of a monolayer of catalyst particles in the direction of the stream, the number of total backmix flow tanks is evidently L/d_p. The relation between the number of such tanks N and longitudinal macrodiffusion D_L, the length of the catalyst bed, and the gas flow rate w is

$$N = \frac{Lw}{2D_L}. \quad (42)$$

When $N = L/d_p$, then $wd_p/D_L = 2$ and the reactor operates as staged total backmix flow tanks.

Fig. 9, which has been constructed on the basis of Carberry's data[40] for a first-order reaction under isothermal conditions, shows the variation of the ratio of the conversion in a stationary bed x_{mix} and the conversion x_{plug} in a reactor without mixing (total plug flow reactor) with the product of the first-order reaction rate constant k and the duration of contact τ. Similar relations have been obtained for non-isothermal and non-adiabatic conditions[42,43].

The relation between the Pe_L number for a plug flow reactor and the number of tanks (or the number of staged reactors) is shown clearly in Fig. 10, based on the data of Trambouze[44].

4. Mixed Models

Apart from the plug and backmix flow streams examined above, additional phenomena occur in real reactors, such as stream circulation, their by-pass flow, cross-over streams, and stagnant zones. The model of the streams in a real reactor is then set up by means of different combinations of ideal backmix flow and plug flow models, stagnant zone models (concentration assumed to be constant),

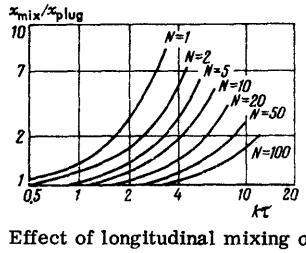


Fig. 9. Effect of longitudinal mixing on first-order processes.

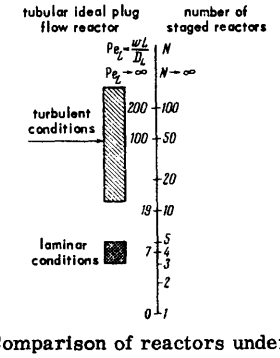


Fig. 10. Comparison of reactors under different hydrodynamic conditions.

etc. Subsequently the output concentration curves for a real reactor are compared with curves constructed on the basis of the proposed combination of models [5]. Table 1, quoted above, is very useful for this purpose.

The simplest mixed reactor models were examined in Levenspiel's monograph [12] and treated systematically by Wen and Chung [19]. The stagnant zone method of calculation, which gives better results than Levenspiel's method, has been described recently [45].

IV. EFFECT OF THERMAL PARAMETERS ON CHEMICAL PROCESSES

The distribution of temperatures in a stream (along the axis t and for radius R) in the presence of a chemical reaction can be represented in the following form, in conformity with the law of conservation of energy:

$$\frac{\partial t}{\partial \tau} = -w\frac{\partial t}{\partial l} + D_{Lq}\frac{\partial^2 t}{\partial l^2} + \frac{D_{Rq}}{R\partial R}\left(R\frac{\partial t}{\partial R}\right) + \frac{w_r(\pm \Delta H)}{c_p\gamma},$$

where $\partial t/\partial\tau$ is the rate of change of temperature with time. If in the system under consideration the heat of chemical reaction evolved is entirely consumed in changing the heat content of the system, the reactor used under such conditions is referred to as an adiabatic reactor. The temperature of the reaction mixture, defined by the ratio $T_a = (\pm\Delta H)c_{A_0}/\gamma c_p$, is then called an adiabatic temperature.

Depending on the model, the following heat balance equations hold for adiabatic reactors:

for a backmix flow reactor

$$V_s\gamma c_p(t_e - t_i) = V_s(c_e - c_i)(\pm\Delta H), \quad (43)$$

for a plug flow reactor

$$V_s\gamma c_p dt = w_r(\pm\Delta H)\,dV_r. \quad (44)$$

The following heat balance equations hold for a polytropic reactor, depending on its model:

for a backmix flow reactor

$$V_s\gamma c_p(t_e - t_i) = V_s(c_e - c_i)(\pm\Delta H) - \alpha F(t_e - t_x), \quad (45)$$

for a plug flow reactor

$$V_s\gamma c_p dt = w_r f(\pm\Delta H)dz - \alpha F'(t - t_x)dz = V_s(\pm\Delta H)dc - \alpha F'(t - t_x)dz. \quad (46)$$

The following notation is used in the above equations: w_γ is the rate of change of concentration due to the chemical reaction, w the linear flow rate, V_s the space velocity of the reaction mass, D_{Lq} and D_{Rq} are the coefficient of longitudinal and radial heat transport, γ is the specific gravity, c_p the specific heat at constant pressure, ΔH the heat of reaction (the plus sign corresponds to an endothermic reaction and the minus sign to an exothermic reaction), t_i and t_e are the initial and final temperatures of the reaction mass, c_i and c_e the initial and final concentrations of the reactants, α is the coefficient of heat transfer from the reaction mass to the cooling agent, t_x the temperature of the cooling agent, F the heat exchange surface area, F' the heat exchange surface area referred to unit length, and f the cross-sectional area of the stream in the reactor.

Isothermal reactors are relatively infrequently used in large-scale processes because of the high cost of the heat-exchange equipment. Therefore adiabatic or polytropic industrial reactors are usually designed.

Cholette and Blanchet [46] made a theoretical comparison of the conversion in an adiabatic plug flow reactor with that in a backmix flow reactor (for a microstate). The comparison yielded the same results for both endothermic and isothermal reactions, i.e. the plug flow reactor proved to be superior to the backmix flow reactor. For exothermic reactions at low conversions, the backmix flow reactor proved to be more convenient than the plug flow reactor, but at high conversions the opposite was true.

The above estimate of the average reaction rates provides an explanation of these findings. The rate of endothermic reactions decreases with the conversion as a result of the consumption of the reactants and the decrease of the temperature of the system. Since the average rate of reaction in the plug flow reactor, where it assumes a value which is the average of the maximum rate at the inlet and the minimum rate at the outlet, is always higher than the average rate in the backmix flow reactor, it follows that in the presence of heat exchange too the plug flow reactor is always preferable to the backmix flow reactor.

The rates of most exothermic processes initially increase with the conversion, as a result of the increasing temperature of the system, but at high conversions they fall due to the consumption of the reactants. Under conditions of increasing rate, the average reaction rate in the backmix flow reactor is always higher than in the plug flow reactor. However, after the attainment of a certain conversion, somewhat higher than that corresponding to the maximum rate, the average rates in both reactor models become identical and at higher conversions the plug flow reactor again becomes more advantageous.

The variation of the conversion with the residence time in plug flow and backmix flow reactor models (at two levels) is shown in Fig. 11 for endothermic reactions and in Fig. 12 for exothermic reactions. In the graphical construction of the conversion profiles, use was made of the temperature variation of the reaction rate based on the Arrhenius equation, and temperature was eliminated by setting up the heat balance for an adiabatic reactor (with subsequent analytical or numerical solution), the following conditions being assumed: $ER/T_0 = 40$ and $T_a/T_0 = 0.1$, where $T_a = (\pm\Delta H)c_{A_0}/\gamma c_p$ is the adiabatic temperature and T_0 the initial temperature.

Comparison of the segregated state with mixing at the molecular level for endothermic reactions (Fig. 11) shows that the highest conversion is attained for reactions of any order in the segregated state. The difference between this result and the result considered for isothermal conditions,

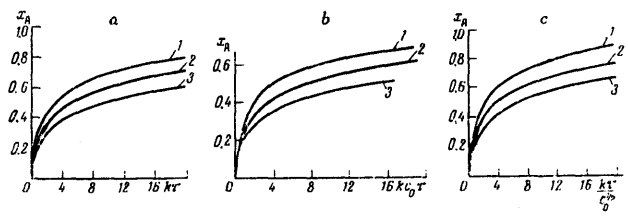


Fig. 11. Dependence of the conversion on the reactor model and the mixing level for endothermic reactions of different orders: *a*) first-order reactions; *b*) second-order reactions; *c*) reactions of order 1/2;
1) plug flow reactor; 2) backmix flow reactor (macromixing); 3) backmix flow reactor (micromixing).

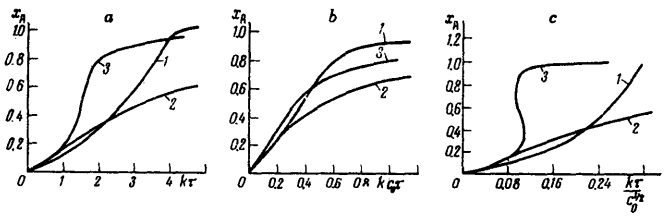


Fig. 12. Dependence of the conversion on the reactor model and the mixing level for exothermic reactions of different orders: *a*) first-order reactions; *b*) second-order reactions; *c*) reactions of order 1/2:
1) plug flow reactor; 2) backmix flow reactor (macromixing); 3) backmix flow reactor (micromixing).

where the order of the reaction has a significant influence, is due to the mode of variation of the reaction rate. In an endothermic system the rate decreases with increasing conversion, both due to the disappearance of the reactants and the decrease of the temperature of the system. In the systems examined above the temperature effect was greater than the compensation due to the order of the reaction.

Comparison of the segregated state with mixing at a molecular level for exothermic reactions (Fig. 12) leads to the opposite conclusion — the highest conversion corresponds to mixing at a molecular level. This is because in exothermic systems the initial rate increases with conversion due to the increasing temperature of the system.

Combinations of reactor models have been considered by Cholette and Blanchet[46]. It was shown that for exothermic reactions a combination of plug flow and backmix flow (at a molecular level) reactors is sometimes more satisfactory than the individual reactor models. Douglas notes[47] that some of Spencer's calculations[48], based on the dispersion model, have shown that the optimum conversion is attained at a certain finite non-zero value of the mixing parameter, i.e. for a hypothetical case intermediate between the plug flow and backmix flow reactor models. These findings can be explained by considering the variation of the average reaction rate in the two systems.

Denbigh[49] showed that the plug flow reactor is always preferable in cases where the rate of reaction decreases with increasing conversion. On the other hand, the backmix flow reactor is more advantageous when the rate increases during the reaction. Therefore, for exothermic reactions whose rate passes through a maximum as the conversion increases, the optimum model is the backmix flow reactor under conditions of increasing rate and the plug flow reactor under conditions of falling rate.

Aris[50] made a quantitative estimate based on the above postulates and showed that, for a reaction of the type A → products,

$$w_r = kc_{A_0}(1-x_A) = c_0^n\left(A\exp\frac{-E/RT_0}{1+\frac{T_a}{T_0}x_A}\right)(1-x_A)^n; \qquad (47)$$

the condition corresponding to the maximum reaction rate w_r is $\partial w_r/\partial x_A = 0$ and the required conversion x at the outlet may be obtained by a combination of backmix flow reactors. The following equation then holds:

$$n\left(1+\frac{T_a}{T_0}x_A\right)^2 = (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \qquad (48)$$

It has been shown that the best model for reversible gas-phase reactions may be obtained by setting up a decreasing temperature profile[51] which can be attained by by-passing a cold feed. Aris[51] examined by-pass schemes with two and three adiabatic reactors and also other optimum schemes.

A comparative assessment of reactor models can be conveniently made by comparing the slopes $dx_A/d\tau$ of $x_A-\tau$ curves, i.e. by differentiating the material balance equations for reactors under different heat-exchange conditions[47]. On the basis of Eqn. (47), we have for the plug flow reactor

$$c_{A_0}^{1-n}\frac{dx_A}{d\tau} = k(1-x_A)^n. \qquad (49)$$

After appropriate substitutions, the material balance equation for the backmix flow reactor yields the expression

$$c_{A_0}^{1-n}\frac{dx_A}{d\tau} = k(1-x_A)^n\left[\frac{1-x_A}{1+(n-1)x_A - x_A(1-x_A)\frac{1}{k}\frac{dk}{dx_A}}\right]. \qquad (50)$$

Comparison of Eqns. (49) and (50) shows that the slope of the $x_A-\tau$ curve for the backmix flow reactor differs from the slope of the curve for the plug flow reactor by the factor

$$\left[\frac{1-x_A}{1+(n-1)x_A - x_A(1-x_A)\frac{1}{k}\frac{dk}{dx_A}}\right]. \qquad (51)$$

Under isothermal conditions we have

$$\frac{dk}{dx_A} = 0,$$

and the factor (51) reduces to the form

$$\left[\frac{1-x_A}{1+(n-1)x_A}\right]. \qquad (52)$$

Since the above factor is always less than unity, the slope of the curves for the total backmix flow reactor is always smaller than the slope for the plug flow reactor and therefore under isothermal conditions the plug flow reactor is always preferable to the backmix flow reactor.

Under endothermic conditions we have

$$\frac{dk}{dx_A} = \frac{d}{dx_A}\left[A\exp\left(\frac{-E/R}{T_0 - T_a x_A}\right)\right] = -\frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1-\frac{T_a}{T_0}\right)^2}. \qquad (53)$$

On substituting Eqn. (53) in Eqn. (51) and assuming that the factor (51) is always less than unity, i.e. that the slope of the $x-\tau$ curves for the backmix flow reactor is always smaller than the slope of the curves for the plug flow reactor, we obtain the inequality

$$-n\left(1-\frac{T_a}{T_0}x_A\right)^2 < (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \qquad (54)$$

Since the left-hand side of this expression is always negative and the right-hand side is always positive, the factor (51) is indeed smaller than unity. Therefore for endothermic reactions a plug flow reactor will always give a higher conversion per unit volume.

For exothermic reactions, we have the equation

$$\frac{dk}{dx_A} = \frac{d}{dx_A}\left[A\exp\left(\frac{-E/R}{T_0 + T_a x_A}\right)\right] = \frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1+\frac{T_a}{T_0}x_A\right)^2}. \qquad (55)$$

It follows from Fig. 12 that the slopes of $x-\tau$ curves for the backmix flow reactor are higher than the slopes of the

curves for the plug flow reactor at low conversions, are equal at a certain intermediate conversion, and lower at high conversions. Therefore on substituting Eqn. (55) in expression (51), we should obtain a factor greater than unity at low values of x and smaller than unity at high values of x:

$$\frac{(1-x_A)\left(1+\frac{T_a}{T_0}x_A\right)^2}{[1+(n-1)x_A]\left(1+\frac{T_a}{T_0}x_A\right)-x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}} \begin{matrix} > 1 \text{ small } x \\ = 1 \text{ intermediate } x \\ < 1 \text{ large } x \end{matrix} \quad (56)$$

or

$$n\left(1+\frac{T_a}{T_0}x_A\right)^2 \lessgtr (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \quad (57)$$

It is evident from formula (57) that at high conversions the right-hand side approaches zero (when x_A tends to unity). At a very low conversion ($x \simeq 0$) the following inequality can be obtained from formula (57):

$$n < \frac{E}{RT_0}\frac{T_a}{T_0}. \quad (58)$$

The inequality (58) is valid for the majority of exothermic systems. It is noteworthy that, if this relation does not hold, the rate of reaction decreases with increasing conversion and the plug flow reactor is more advantageous than the backmix flow reactor.

To determine the optimum combination of reactor models, consider the graphical method based on the construction of a conversion profile [46,47,52]. On the basis of Fig. 12, characterising the conversion profile for individual reactor models, one constructs a conversion curve for exothermic reactions in the backmix flow reactor (Fig. 13, curve *1*) which gives the steepest possible curve. If a system comprising a combination of two reactor models (backmix flow–plug flow) is proposed, a second curve for the plug flow reactor must be constructed (curve *2*). The point A corresponding to the highest slope of the curve for the backmix flow reactor is selected. The line AB, parallel to the curve for the plug flow reactor along the section CD, is drawn from point A. The line AB characterises the conversion which obtains for the combination of the two reactors. However, this profile does not yield the optimum system, because evidently best conditions can be achieved if the system includes a larger backmix flow reactor and a smaller plug flow reactor. Similarly if the conditions of the backmix flow reactor correspond to those at point G and a profile is constructed for the combined system, better conditions can be attained in a system with a smaller backmix flow reactor. Therefore under the conditions at point

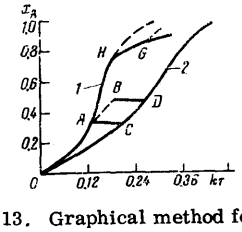


Fig. 13. Graphical method for the construction of combined reactor models:
1) backmix flow reactor (micromixing); 2) plug flow reactor.

H (the point corresponding to equal slopes of the curves) the optimum reactor combination is obtained.

Thus the following conclusions can be arrived at on the basis of the above considerations: the ideal plug flow reactor is always more advantageous for isothermal and endothermic conditions, while for exothermic conditions a combination of reactor systems is more suitable. The optimum temperature profile for complex reactions has been examined by Bilous and Amundson [53]. Slin'ko [54] calculated optimum temperature profiles for contact-catalytic reactors.

V. THERMAL STABILITY OF CHEMICAL REACTORS

The concept of the stability of systems was first formulated by Lyapunov [55]. A system is regarded as stable if after the removal of any perturbation it returns to the previous state. When thermal stability of chemical reactors is considered, perturbations can arise in the system in exothermic processes due to the different mode of heat supply and heat removal. The thermal stability of chemical reactors has a significant effect on the temperature and concentration profiles in the reactor and also provides information which can be used in the selection of the automatic reactor control system.

Assuming that the heat gained by the reactor is evolved in the chemical reaction, i.e.

$$dQ_{\text{infl}} = w_r \Delta H\, dV_r = k_0 e^{-E/RT} c_{A_0}^n (1-x_A)^n \Delta H\, dV_r \quad (59)$$

and the heat loss is determined by the heat content change in the system and by an external heat exchanger,

$$dQ_{\text{outfl}} = V_s \gamma c_p\, dt + \alpha F' (t - t_x)\, dz \quad (60)$$

it is readily seen that the relation between the heat gained and the temperature of the system is exponential, while that between the heat lost and the temperature of the system is linear, i.e. in an exothermic reaction the rate of heat gain is much faster than the rate of its loss and can result in an undesirable increase in the temperature of the system. This fact was pointed out at one time by Semenov [56] and Frank-Kamenetskii [57]. Under endothermic conditions, the problem of stability does not arise.

The necessary condition for the stability of the reactor with respect to heat is

$$\frac{dQ_{\text{outfl}}}{dT} \geqslant \frac{dQ_{\text{infl}}}{dT}. \quad (61)$$

It follows from the heat-exchange conditions in different reactor models examined earlier that the stability conditions also depend on the reactor model and the degree of conversion in the system.

A characteristic feature of the temperature profile of a tubular plug flow reactor with an external heat exchanger is that the reaction volume is proportional to the square of the diameter, while the surface area of the heat exchanger is proportional to the diameter. Therefore in tubes of large diameter the instability is more pronounced than in tubes of small diameter.

As the process proceeds in a plug flow reactor, the temperature initially rises fairly rapidly and the rate of heat loss also increases. The maximum temperature is attained at the point where the local rate of heat loss is equal to the rate of heat supply as a result of the reaction. With increasing conversion, the reaction rate falls, which leads to

a decrease of the temperature in the reaction zone, the temperature approaching that of the cooling agent. Only for a reaction of zero order, whose rate is independent of concentration, does the temperature in the reactor remain constant at the maximum value until the reaction is complete. It should be borne in mind that, with the exception of autocatalytic reactions and reactions with an induction period, the maximum reaction rate at a given temperature is the initial rate, i.e. the rate at the inlet to the reactor, where in fact there is a risk of a sharp rise of temperature.

The stability criteria can be found directly from the balance equations examined previously. According to Eqns. (10) and (49), the following expression is valid for an exothermic first-order reaction in an ideal backmix flow reactor of fixed volume:

$$x_A = k\tau(1-x_A). \tag{62}$$

The requirement for stability is[61] that the derivative of the left-hand side of Eqn. (62) with respect to x_A should be greater than the derivative of the right-hand side, representing the heat gain. Then, in conformity with Eqn. (55), we have the inequality

$$1 > -k\tau + \tau(1-x_A)\frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1+\frac{T_a}{T_0}x_A\right)^2}. \tag{63}$$

Using Eqn. (62), the product $k\tau$ can be eliminated from the last expression and the stability criterion is obtained in the form[47]

$$\frac{\left(1+\frac{T_a}{T_0}x_A\right)^2 - x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}}{(1-x_A)\left(1+\frac{T_a}{T_0}x_A\right)^2} > 0. \tag{64}$$

We may note that when the stability condition is defined by the inequality (64), the inequality (57) becomes unambiguous.

If condition (64) is satisfied for all conversions, the so-called global stability obtains. The relations between the parameters E/R, T_a, and T_0 can then be found. For this purpose, it is necessary to know the values of x_A at which condition (64) is minimised.

Let

$$h = \left(1+\frac{T_a}{T_0}x_A\right)^2 - x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0} > 0. \tag{65}$$

The value of x_A for which h is a minimum can be found from the condition $\partial h/\partial x_A = 0$:

$$x_{A_{min}} = \frac{\frac{E}{RT_0}-2}{2\left(\frac{T_a}{T_0}+\frac{E}{RT_0}\right)}. \tag{66}$$

On substituting Eqn. (66) in Eqn. (65), we obtain

$$h_{min} = \frac{\frac{E}{RT_0}\left[1+\frac{T_a}{T_0}\left(\left[1-\frac{1}{4}\frac{E}{RT_0}\right)\right]\right.}{\frac{T_a}{T_0}+\frac{E}{RT_0}}. \tag{67}$$

The stability of the ideal backmix flow reactor has been analysed by Van Heerden[58], who was the first to show that several stable states are possible. Bilous and Amundson[59] made a quantitative analysis of stability criteria on the basis of the equation for the non-steady state. Aris and Amundson[60] analysed the stability of the ideal backmix flow reactor without a regulator and also with a proportional regulator, which enhanced the stability. The results of the analysis were presented in the form of phase diagrams in terms of dimensionless concentration–temperature coordinates. The stability of the ideal plug flow reactor has also been analysed by Van Heerden[58].

The stability conditions for a semicontinuous reactor with a stirrer, taking into account the residence time of the reaction mass in the reactor, were formulated by Kafarov and Eremenko[61]. They also indicated scaling methods for reactors of different dimensions, with maintenance of stability conditions, which is very important in industrial practice.

Simchen[62] obtained a solution in the form of the transcendental equation $\exp(-E/RT) = a(T - T_w)$ (where a is a constant depending on the physical parameters of the system) for temperatures corresponding to the points of intersection of the heat gain and heat loss lines, taking into account the temperature of the reactor walls T_w.

The maximum permissible temperatures for a given conversion and selectivity in stirred reactors for parallel and consecutive reactions have been examined by Westerterp[63]. The practical difficulties encountered in the attempts to attain the required process temperature were demonstrated, using the synthesis of phthalic anhydride as an example. Liu Shean Lin and coworkers[64,65] analysed the stability of adiabatic and non-adiabatic reactors with a stationary catalyst bed. The mathematical model was reduced to an examination of the behaviour of the individual particles immersed in the gas stream, when the resistance to heat and mass transport is concentrated on the surface of the particles. An irreversible first-order reaction in the absence of longitudinal and radial gradients of gas flow rates was considered. The balance equations were solved numerically by the response curve method and a graphical interpretation of the solutions was given. The following findings were obtained for the adiabatic reactor. In the initial sections of the bed the stable state is attained relatively rapidly, compared with the output from the bed. At low temperatures the difference between the temperatures and concentrations in the gas and solid phases is almost negligible. These are kinetic conditions, since at low temperatures the chemical reaction is very slow. When the temperature of the particles is relatively high, the chemical reaction is accelerated and heat is rapidly evolved. The process becomes diffusion-dependent. A considerable difference between the concentrations and temperatures in the gas and solid phases then arises.

At a relatively low temperature of the gas at the inlet, the chemical reaction virtually does not take place via the bed and the concentration and temperature profiles are planar. On raising the gas temperature at the inlet, the conversion increases rapidly, becoming almost complete at a certain temperature (the temperature gradient in the bed is then almost zero). The higher is the concentration (partial pressure) of the component at the inlet to the bed the higher is the temperature of the exit gas and the chemical reaction is completed over a relatively short length of the bed. Different profiles are possible for the same temperature and concentration at the inlet and the system may be unstable, depending on the existence of local steady states and their multiplicity for individual particles.

If each particle along the axis of the bed had only one steady state, the reactor would be stable and there would be unique concentration and temperature profiles for all the initial temperatures and particle concentrations.

Due to the heat transmitted via its walls, in a non-adiabatic reactor there is instantaneous radial heat and mass transport in the reactor itself. The temperature within the bed can then be lower than the temperature of the inflowing gas and therefore under non-steady conditions the state of the particles may be different than in the adiabatic reactor. The temperature profile changes sharply as a result of slight change in the temperature of the gas at the inlet. The temperature and concentration profiles vary markedly with the coefficients of heat transfer from the particles in the bed to the gas and from the gas to the reactor walls. Furthermore, as in the adiabatic reactor, there is a possibility of the occurrence of non-unique temperature and concentration profiles, depending on the presence of a multiplicity of states for individual particles. The stability of the system is affected by the initial conditions, such as the initial temperature of the particles of the bed, the temperature of the inflowing gas, and the partial pressure of the reactant. These findings[64,65] agree with earlier investigations[66-68]. Barkelew analysed the stability of reactors with a stationary bed by introducing empirical dimensionless parameters[69].

The stability of contact-catalytic reactors was analysed in the widely recognised work of Boreskov[3], Slin'ko[54], Beskov[70], and others. In these studies the stability conditions were formulated, whereby it is possible to calculate the maximum permissible tube diameters in contact-catalytic apparatus for various synthetic processes. It has been shown that the contact-catalytic unit, consisting of two stable reactors, can have unstable states. The problems of the optimisation of the contact-catalytic apparatus for industrially important processes such as the oxidation of sulphur dioxide, ethylene, methanol, and others were also developed in these investigations.

Kafarov et al.[71] provided a mathematical foundation for the stability criterion. Approximate stability conditions were found[72] for a non-continuous ideal backmix flow reactor with regulation of the coolant temperature and the rate of reactant injection and also for the load period of a semi-continuous reactor with regulation of the coolant temperature. One of the possible ways of increasing the stability of the process in chemical reactors, consisting in setting up an automatic control system for the coolant temperature in the refrigerator and for the rate of injection of reactants as a function of the temperature of the reaction mass, was demonstrated.

Using Lyapunov's method, a number of investigators[60,73-75] analysed the stability of a reactor in the presence of non-continuous perturbations and various control systems. Hoftyzer and Zwietering[76] investigated the stability and control of the ethylene polymerisation process and established that, for certain versions of the set up, there are five possible solutions corresponding to stable states. The stability of chemical reactors for two-phase systems, taking into account the possibility of regulation, was investigated by Schmitz and Amundson[77]. Later Amundson and co-workers[78,79] developed mathematical methods for the analysis of the stability of tubular reactors.

VI. EFFECT OF DIFFUSION PARAMETERS ON CHEMICAL PROCESSES

Depending on the effect of *diffusion macrofactors*, chemical processes can be divided into (1) chemical processes under "kinetic" conditions, (2) chemical processes under diffusion-dependent conditions, and (3) chemical processes under mixed conditions.

A characteristic feature of chemical processes under kinetic conditions is that the rate of the chemical reaction itself is slowest, limiting the rate of the process as a whole, while the flow rates of the streams and their physical properties do not influence the process appreciably. In chemical processes under diffusion-dependent conditions the rate of diffusion of reactant to the reaction zone is rate-limiting and depends on the flow rates of the streams and their physical properties. A characteristic feature of processes occurring under mixed conditions is that the rates of chemical reaction and diffusion are comparable.

The possibility, in principle, of isolating the rate-limiting stage is based on the fact that in many cases a complex process consists of several consecutive stages. The slowest rate is rate-limiting. The methods available for the determination of the rate-limiting stage of the process, i.e. of determining whether diffusion-dependent or kinetic conditions predominate, are as follows[80].

1. Determination from the temperature coefficient of the overall rate of the process. If on changing the temperature by 10 deg the overall rate of the process changes by a factor of 2-3, then, as a rule, the chemical reaction itself is the rate-limiting stage. On the other hand, if a 10 deg temperature change entails a change in the rate of the process by a factor of less than two, mass exchange is the rate-limiting stage. In intermediate cases the reaction takes place under mixed diffusion-dependent and kinetic conditions.

2. Determination from the apparent order of the reaction. If the order is not unity, the rate-limiting stage is the chemical reaction. However, if the order is unity, the question of the rate-limiting stage remains open, since the mass exchange process is also directly proportional to the concentration.

3. Determination from the variation of the overall rate of the process with its hydrodynamic conditions. If the rate of the process is independent of the hydrodynamic conditions, the rate-limiting stage is either mass exchange or simultaneously mass exchange and the chemical reaction (i.e. the reaction takes place under mixed diffusion-dependent and kinetic conditions).

Under diffusion-dependent conditions the rate of the reaction, like the diffusion coefficient, varies relatively little with temperature but changes with the flow rate of the gas stream, like the Nusselt diffusion number[16], i.e. is proportional to the gas flow rate raised to the power of 0.4-0.5 for outside flow and to the power of 0.8 for turbulent motion in inside flow.

Under diffusion-dependent conditions the rate of reaction in no way depends on the concrete features of its chemical mechanism; the rates of a wide variety of reactions differ only because of differences in the diffusion coefficients of the reactants and in the case of reversible reactions because of differences in the equilibrium conditions. All the reactions under diffusion-dependent conditions are of first order with respect to the reactant concentration at a constant total pressure. The order of the reaction with respect to the total pressure differs from the order with respect to the concentration.

Diffusion-dependent conditions obtain at high reaction rates and low rates of diffusion, i.e. at high temperatures, high pressures, and low gas flow rates. On the other

hand, at low temperatures, low pressures, and high gas flow rates, kinetic conditions obtain. In the intermediate region mixed diffusion-dependent and kinetic conditions obtain, where the effect of both diffusion and reaction kinetics is significant. The effects of chemical reactions and diffusion can be taken into account quantitatively (using the additivity principle) and simultaneously only for linear systems, i.e. first-order reactions. The solution of non-linear problems usually reduces to finding a rate-limiting stage in the process.

Examination of the model of the contact-catalytic chemical process from the standpoint of transport phenomena shows that the process takes place simultaneously at microscopic and macroscopic levels. Axial and radial dispersion of heat and mass between the particles, transport of heat and mass between the phases, and transport within the particles take place. Much work has been done in recent years on the study and analysis of transport phenomena in contact--catalytic processes. Since these studies cannot be considered here, the reader is referred to two detailed reviews on this topic [40,81] and also to recent monographs [82,83].

The studies of chemical processes on free surfaces in gas–liquid, vapour–liquid, and liquid–liquid systems have been attracting increasing attention in recent years. The so-called "extractive" reactions, involving the addition of an immiscible solvent to a homogeneous system during chemical reaction in order to remove a side-product or the required product, have been finding increasing application in chemical industry. The chemical process and extraction are carried out continuously [84-87]. A similar principle is used in the application of absorption and fractionation [88]. The effect of mixing on the chemical reaction in liquid–liquid and gas–liquid systems, which is important under these conditions, has been studied by a number of investigators [89-93]. It has been shown that, in a reaction system with mixing, physical equilibrium between the phases may not be attained.

In the construction of mathematical models of chemical processes in two-phase systems, usually one of two possible models is adopted for each phase: the model with centralised parameters and the model with distributed parameters. The model with centralised parameters includes one independent variable, namely time. In models with distributed parameters the variation of variables with time and space is considered, which leads to partial differential equations. The mixing process in homogeneous systems can be described by the model with centralised parameters with an accuracy which is satisfactory for practical purposes. In heterogeneous systems the model with centralised parameters can be applied to the continuous phase and the model with distributed parameters to the disperse phase. In contact-catalytic processes with a solid phase, the catalyst may be regarded as a disperse phase. On the other hand, if the disperse phase is a liquid, the occurrence of internal circulation, coalescence, and redispersion permits the assumption of ideal mixing within the limits of each drop and therefore the model with centralised parameters may be applied to both phases.

However, in a disperse phase account must be taken of the scatter of the values of the dependent variables, i.e. of the presence of a definite distribution of the medium particles (drops) with respect to the residence time (the "age"). If, on the other hand, the drops coalesce and undergo redispersion at a very high rate, the distribution may be evened out. This is most likely for two liquid phases and less likely if the disperse phase is a gas. In practical calculations, it is usually assumed that there is no definite distribution in the disperse phase.

In the construction of mathematical models, one of the following schemes is adopted: (1) the rates of heat and mass transport between the phases are high and the rate of conversion is rate-determining or (2) the rates of transport at the interface are high and therefore the system is in physical equilibrium. According to the second scheme, mass transport is rate-determining, i.e. under these conditions the rate of reaction is so high that the course of the process as a whole is determined by the rate of transport of the reactants. The reactants and the reaction products in the reacting phase are in chemical equilibrium and their concentration in this phase is defined by an equilibrium constant. In intermediate cases the concentrations do not correspond to equilibrium relations and the temperatures of the phases are not the same, and therefore it is then necessary to take into account all the rates of the process.

Various combinations of the above models are possible in cases where the reactions take place at different rates in one or two phases. For example, the reaction may be so fast in one phase that the reaction components are in chemical equilibrium, and the overall rate of reaction is then determined by the conversion in the second phase. More complex situations can also arise in the presence of consecutive, parallel, and other complicated reactions. A number of problems of this kind have been examined in the work of Schmitz and Amundson [77] (quoted previously), who investigated the conditions of stability and control in reactors with stirred two-phase systems. A number of studies on the attainment of conditions corresponding to the occurrence of reactions on free surfaces in liquid-phase systems have been made by Abramzon and coworkers [94]. The studies on chemical reactors for gas–liquid systems have been reviewed by Teller [95].

The effect of circulation on chemical processes and calculations on circulation systems have been described in Nagiev's monograph [96]. Calculations on contact-catalytic processes taking into account circulation are quoted in Orochko's monograph [97] and in a number of later papers of Zinov'eva and Orochko [98]. They also consider the effect of heat and mass transport on chemical reactions.

The general method for the construction of mathematical models for complex chemical reactions which allow the calculation, with the aid of analogue computers, of the kinetic characteristics of reactions of any order taking into account the non-isothermal conditions of the process, and also the calculation of the parameters of reactor control systems, has been described by Biryukov and Kafarov [99]. They also described the ideas underlying the element-by-element calculation by analogue computers of the parameters of various models of industrial chemical reactors [100-102].

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GAS CHROMATOGRAPHY IN CATALYTIC STUDIES

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I. INTRODUCTION

The development of gas chromatography opens up wide possibilities in the study of catalytic processes. Gas chromatography makes it possible to obtain in a relatively short time information about the composition of the starting materials and products in catalytic processes, facilitates tests on catalysts, and greatly simplifies the experimental technique. A number of examples have been described of the successful use of gas chromatography in the analysis of the products of catalytic processes such as hydrogenation [1-5], dehydrogenation [6-8], isomerisation [9-12], dealkylation [13-15], oxidation of organic and inorganic substances [16-18], polymerisation [19-21], and reactions of organosulphur compounds derived from petroleum [22-24] and of other substances.

In many cases the method in which the catalytic reaction is performed in a flow microreactor attached directly to a chromatographic column proved very fruitful [25-29]. The use of labelled atoms in radiochromatography has been an effective means of studying the mechanism of catalytic processes [28,30,31].

Considerable interest attaches also to catalytic reactions under chromatographic conditions [30-33], whereby it is possible to obtain rapidly new, valuable data on the mechanism and the kinetics of the process and on the properties of the catalyst and their variation with time.

Finally, gas chromatography is a rapid method for the determination of the isotherms and heats of adsorption, the specific surfaces of catalysts, and their surface structure, acidity, and catalytic activity [34-39].

II. QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE PRODUCTS OF CATALYTIC PROCESSES

The study of the majority of catalytic processes is impossible without qualitative and quantitative analysis of the initial materials and the reaction products. In these studies gas chromatography often proves to be the most effective analytical method both in laboratory tests and in the control of industrial processes [40-44].

The methods of analysis of the products of catalytic processes must as a rule meet very stringent requirements, particularly if the reactions are fast and rapid analysis is necessary. For this reason, the shortening of the duration of analysis while maintaining adequate capacity for separation and adequate precision is one of the principal requirements which must be satisfied by a gas-chromatographic method. In many catalytic processes very complex mixtures of substances of different types are obtained, the concentrations of the individual components varying between very wide limits [6,40,41,45]. It is very difficult to separate such mixtures and to analyse them qualitatively and quantitatively.

On the other hand, the determination of trace impurities in the starting materials or the catalytic reaction products is no less complex a problem [46]. The total analysis of the products is frequently interfered with by the presence in the latter of unstable or reactive compounds, substances tending to polymerise, and also water [16,47-49]. It is therefore often necessary to perform extensive preliminary experiments in order to find the most favourable conditions for the chromatography of such mixtures.

Qualitative analysis. Qualitative analysis in gas chromatography is usually concerned in the first place with

the determination of the retention time (or volume)[50-54]. Several methods are known for the identification of chromatographic peaks, based on the measurement of these quantities: (1) determination of the relative retention volumes of the substances being analysed and the pure compounds, in relation to some standard, on several liquid phases; (2) the use of the variation of the logarithm of the retention volume of the given substance with the number of carbon atoms, which is linear within a homologous series; (3) determination of the relation between the logarithm of the retention volume and the factor $Z = T_b/T$, where T_b is the boiling point of the substance and T the column temperature; (4) the use of retention indices (the Kováts method).

Until recently the first method was most frequently employed. A large number of tables and individual data on the relative retention volumes of substances of a wide variety of classes of various liquid phases and adsorbents have been published[50-54]. However, the use of these data is difficult because different workers have used different substances as standards and have made measurements at different temperatures, as a result of which the data are often inconsistent[55].

More reliable results are provided by plots of the logarithms of the retention volumes against the number of carbon atoms or against the boiling points of substances within a single homologous series at a given column temperature. Extensive experimental data on the identification of the homologues of various classes of organic compounds on eighteen liquid phases have been presented by Tenney in the form of such graphs[56].

Zhukhovitskii and Turkel'taub[53] proposed to use the relation between the logarithm of the retention volume of a given substance and the factor Z, defined as the ratio of the boiling point of the substance and the column temperature. For members of a single homologous series, this relation is approximately linear. The identification reduces to finding the boiling point of the test substance from the plot and comparing it with tabulated data. An advantage of this method of identification is that it permits measurements at different temperatures, which is inevitable when the mixture contains components with sharply different boiling points.

Recently the retention indices proposed by Kováts[57-61] have been receiving an increasing amount of recognition. This method of qualitative identification is based on the use of the familiar relation between the logarithms of the retention volumes and the number of carbon atoms in straight-chain paraffins, the logarithms of the retention volumes of such straight-chain paraffins being adopted as an index I scale. In this scale the retention indices for straight-chain hydrocarbons are assumed to be equal to the number of carbon atoms multiplied by one hundred and the indices of other substances, which have intermediate values, are found from the formula

$$I = 100\frac{\ln V_R - \ln V_{R(n\text{-}C_n)}}{\ln V_{R(n\text{-}C_{n+1})} - \ln V_{R(n\text{-}C_n)}} + 100n,$$

where V_R is the true retention volume of the test substance (i.e. the retention volume corrected for the dead space in the column), $V_{R(n\text{-}C_n)}$ the true retention volume of a straight-chain paraffin with n carbon atoms, and $V_{R(n\text{-}C_{n+1})}$ the true retention volume of a straight-chain paraffin with $n + 1$ carbon atoms; we have

$$V_{R(n\text{-}C_n)} \leqslant V_R \leqslant V_{R(n\text{-}C_{n+1})}.$$

The method of expressing the retention volumes in the form of indices has a number of advantages, the most important of which are as follows.

1. The standard is not a substance selected at random but the homologous series of straight-chain hydrocarbons, which enhances the precision of the determination of the indices, and the latter can be reproduced in other laboratories with greater reliability.

2. The difference between the retention indices for a single substance on two liquid phases, polar and non-polar, characterises its chemical nature, which facilitates the qualitative analysis. At the same time, this difference can serve as a quantitative characteristic of the polarity of the chosen liquid phase.

3. When literature data on the retention indices are available, qualitative analysis without pure substances is possible, which is of considerable interest in the analysis of multicomponent mixtures of unknown composition[61].

4. The Kováts indices vary with temperature much less than the simple relative retention volumes, which facilitates the use of literature data obtained at different temperatures[62].

The system of Kováts indices is probably the most universal and the most promising, as evidenced by the fact that an increasing number of investigators have used them in their studies. At the present time tables of retention indices are being compiled for substances of different classes on a wide variety of liquid phases[58,60,63]. In the determination of the retention indices it is essential to exclude as far as possible the effect of adsorption on the solid support, which is particularly pronounced in the chromatography of polar substances[64,65]. In this connection the work carried out to find new supports and to improve the properties of the commonly used inert supports merits attention[66-84]. The technique of liquid phase deposition also has an important role[85].

In the study of new catalytic processes, whose products consist of complex mixtures of unknown composition, it is desirable to check the results of identification based on the retention time or volume by another independent method. Infrared spectroscopy and mass-spectroscopy have found very wide application recently in the analysis of fractions emerging from gas-chromatographic columns[1,86-99]. The combination of gas chromatography with nuclear magnetic resonance is of considerable interest. For example, using this combination of methods, it proved possible to identify the products of complex catalytic processes, such as the condensation of isobutene with formaldehyde[45] and others[100,101]. Examples of the application of polarography in the analysis of fractions eluted from the chromatograph have also been described[102].

In the analysis of complex mixtures preparative gas chromatography, in which considerable advances have now been made[103-107], may prove very useful. Frequently in the identification of chromatographic peaks use is made of chemical reactions specific to pure substances or classes of substances, which are carried out either with the initial mixture to extract or convert a number of products or with fractions collected at the outlet from the chromatograph[108-112]. A method of carrying out such reactions directly in the injector containing the test sample in the vaporised state has been described[109,110].

Chemical reactions can also be conveniently performed in a reactor connected to the chromatograph and the carrier

gas source. The reactor is filled with a suitable reagent or catalyst and maintained at a specified temperature, the reactants being introduced with the carrier gas. For example, in the qualitative analysis of substances of different classes the latter may be catalytically hydrogenated to the corresponding hydrocarbons, which are more readily identified [113-116].

Dravert and other investigators [117-121] extended the range of reactions which can be carried out in a microreactor — they converted the starting material into ethers, saturated and unsaturated hydrocarbons, etc. They showed that this method (which they called reaction chromatography) is not only a means of qualitative analysis but can also be used for quantitative determinations. In many cases it leads to a simplification of the chromatographic process, particularly if the mixture to be analysed contains high-boiling polar substances (for example, alcohols, glycols, acids, hydroperoxides, etc.) [122,123].

A number of workers [124-126] have used pyrolysis with subsequent chromatographic analysis of its products for the qualitative identification of the components of complex mixtures and the analysis of complex organic substances and polymers. The resulting chromatograms are compared with the chromatograms of the pyrolysis products of the substances which are expected to be present. The chromatogram of the pyrolysis products of a compound constitutes a characteristic spectrum, resembling the mass spectrum. The ratios of the peak intensities (heights) may serve as a qualitative characteristic of a given substance.

The literature on reaction chromatography, including pyrolysis, has been reviewed by Berezkin and Gorshunov [127].

Quantitative analysis. Quantitative analysis in gas chromatography is based on the calculation of chromatograms. There are several methods of calculation, depending on the parameters of chromatographic peaks used [53,128]. In practice, the peak area is normally employed as the parameter in the calculation. A number of methods have been described for the determination of peak areas [53,129-134]. In order to obtain accurate quantitative results, it is important to choose the most suitable method for each particular case, depending on the magnitude and shape of the chromatographic peaks. It should also be noted that the use of integrators greatly facilitates the measurements and yields accurate results when all the peaks in the chromatogram are fully separated, regardless of their shape [135-137]. When the separation is incomplete, quantitative analysis based on a detailed study of the shape of the peaks and the mode of their superposition is possible. Several methods for the calculation of incompletely resolved peaks have been described [134,138].

The ratio of peak areas is usually not the same as the ratio of the concentrations of the mixture components. In the first place, this is due to the different sensitivities of the detector to different substances and in the second place to the non-linearity of the detector response. The effect of these factors on the results of quantitative analysis can be taken into account by means of calibration against pure substances and artificial mixtures. Usually three methods of calibration are employed: the method of absolute calibration, the method of internal normalisation (taking into account the coefficients of the sensitivity of the detector to different components), and the internal standard method. The applicability of a particular method depends on the qualitative composition of the mixture to be analysed, on the concentration ratios of its components, on the properties of the detector (the range of linearity, sensitivity, etc.), and certain other factors. This problem has been adequately treated in monographs on gas chromatography [53,54,128] and in the recently published review of Andreev et al. [134], where molar correction coefficients for substances of different classes and detectors of different types have been tabulated.

In the analysis of the products of catalytic processes, both under laboratory and industrial conditions, the problem of the choice of the correct method of sample injection into the chromatograph frequently arises, since it determines the quality of the separation and the reproducibility of the quantitative results [53,139]. At the present time gaseous samples with accurately specified volumes can be most readily introduced by means of dosimetric taps of different designs [128,140-142]. For this reason, an attempt is often made to meter out the liquid samples in the vapour phase. The problem then reduces to the design of sampling taps which would remain gas-tight at an elevated temperature (to prevent the condensation of the mixture components) and which would ensure the required reproducibility of the metering [142-144]. When such taps are present, vaporised mixtures of products of catalytic processes can be analysed directly at the outlet of the reactor without preliminary condensation and trapping, which greatly shortens the duration of the analysis and simplifies the experimental method.

Liquid and solid samples are usually introduced by means of microsyringes, micropipettes, sealed tube breaking devices, and certain other procedures [54,145-147]. All these methods have a number of disadvantages which must be taken into account in the experiments to reduce their effects. Among all the devices, microsyringes are preferred [148]. Reactive substances are introduced in sealed tubes [145].

Let us now consider briefly the methods of accelerating gas-chromatographic analysis, since frequently the duration of the study of a catalytic process is determined by the rate of analysis of its products. The problem of the acceleration of chromatographic separation is indissolubly linked to the efficiency of the column, the selectivity of the liquid phase or the adsorbent, and also the retention time. In many cases involving a high degree of separation the duration of analysis may be shortened by decreasing the proportion of liquid phase, by increasing the temperature of the column and the flow rate of the carrier gas, and by using as the latter hydrogen or helium which have low viscosities [149,150].

The separation of multicomponent mixtures over a wide range of boiling points of the components is greatly improved if the column temperature is increased during the analysis, which is achieved by temperature programming [151-153] and by a chromathermographic technique [53,154,155]. To shorten the duration of analysis, it is convenient to use surface-porous adsorbents and carriers, with pores only at the surface itself, for example porous glasses [156], glass microbeads which have been etched or covered by a layer of a highly dispersed substance [75,157], and other materials. The analysis can be greatly accelerated by decreasing the column diameter [158] and by employing capillary chromatography [53].

Apart from reducing the time of separation, chromatography at reduced pressures provides more favourable separation conditions. It is then possible to reduce considerably the column temperature (since the volatility of the components increases), which enhances the selectivity of the liquid phase and analysis of thermally unstable substances becomes possible [159-161]. Reaction gas chromatography may be used for

the same purpose, whereby high-boiling polar substances can be converted into readily volatile compounds [117-119].

A number of workers have attempted [162,163] to calculate theoretically the minimum time for analysis in capillary and packed columns. Examples of the separation of multicomponent mixtures during the periods of the order of one minute have been given. The chromatograms are recorded with the aid of an oscilloscope [150].

III. CATALYTIC PROCESSES IN A MICROREACTOR (RADIOCHROMATOGRAPHY). THE STUDY OF CATALYTIC REACTIONS UNDER CHROMATOGRAPHIC CONDITIONS

The advantages of the gas-chromatographic method of analysis are most fully shown in the study of catalytic processes in a microreactor attached directly to the separating column of the chromatograph. Either inert gases or gaseous starting materials (H_2, O_2, and others) are used as the carrier gas. The remaining starting materials are introduced into the reactor periodically and are transferred by the carrier gas through a layer of catalyst into the chromatographic column, where the products and the unreacted components of the initial mixture are separated. By carrying out the process in a microreactor, it is possible to investigate over a short period the activity and selectivity of a large number of catalysts while varying various parameters (temperature, space velocity, pressure, etc.) [28,29,164-166].

Catalytic processes in a microreactor are as a rule fast and analysis of the products is the rate-limiting stage in the investigation of reactions and catalysts. For this reason, gas chromatography, which is one of the fastest analytical methods, is the most convenient in this case. In the study of catalytic processes in a microreactor, it is essential to exclude possible analytical errors due to, for example, the sorption of substances on the catalyst, the non-identity of the conditions obtaining in the calibration and in the analysis, the inadequacies in sample injection, etc. It is essential to achieve satisfactory reproducibility of the quantitative chromatographic analysis, since in each experiment it is possible to obtain only one chromatogram. At the present time the system comprising a chromatograph with a microreactor is widely used in the study of both the catalysts themselves [167] and various catalytic processes: hydrogenation and dehydrogenation [25,26], oxidation [27,168], cracking [28], polymerisation [19], and others.

In the study of the molecular mechanism of reactions, tracer atoms and radiochromatography may prove very useful. The essential feature of radiochromatography is the addition to the initial mixture of one of the components which is radioactively labelled. The products of the catalytic reaction are separated and analysed in a chromatograph with two detectors connected in series, for example a katharometer and a radiometric cell. Comparison of the chromatograms obtained with the aid of the two detectors shows which products can be obtained from the substance labelled with a radioactive isotope [28,169]. If a labelled substance, which according to the postulated possible mechanisms of the process is an intermediate, is added to the starting materials, then, by measuring the specific activity of the final products, it is possible to investigate the mechanism and kinetics of the individual stages of the reaction (Neiman's method) [170-172]. Such investigations are usually performed using a microcatalytic apparatus, since the study of the process in a microreactor requires only small amounts of the starting materials. Of course, the results obtained in a microreactor cannot describe the process as a whole. The selectivity of the catalyst may change on going to larger apparatus. It is also possible that under conditions obtaining in the microreactor optimum operation of the catalyst is not always achieved and therefore caution must be exercised in approaching the problem of catalyst selection on the basis of such data alone. However, microcatalytic apparatus with chromatographs can be used successfully in the study of the mechanism of catalytic processes.

Catalytic reactions under chromatographic conditions are more specific. This method is used in the study of both various types of reaction and of the changes in the catalysts during the experiments (exploitation, poisoning, and regeneration) [30-33,173,174]. A microreactor with a catalyst is also used in catalytic reactions under chromatographic conditions. The starting material is introduced as a separate sample (pulse) into the reactor and is transferred by the inert carrier gas or by a gaseous reactant to a layer of catalyst. The reaction products and the starting materials are separated on the catalyst itself and are analysed at the outlet from the reactor by means of a suitable detector.

The conditions of catalytic reactions in pulse chromatography differ from those usually encountered. Thus under chromatographic conditions the intermediate and final products are separated from the starting materials and therefore the interactions between them and the reverse reactions are almost completely excluded. The conversion then increases sharply. In those cases where any one product is not separated from the starting material on the catalyst, it is possible to investigate the process with the latter inhibited by its products and to assess the effect of such inhibition.

Furthermore, under chromatographic conditions the reactants are freed from impurities (except for the impurities present in the carrier gas), which may be catalyst poisons, inhibitors, promoting agents, or initiators. The effect of these impurities can also be investigated [173].

The characteristic features of the chromatographic conditions make it impossible to use this method to investigate the reactions of two or more starting materials in an inert carrier gas, since, as a result of the chromatographic separation of the initial mixture, the reactant molecules do not meet either in the gas phase or on the catalyst surface.

The chromatographic conditions can be conveniently used for reactions of the type

$$A \rightleftarrows B + C,$$

which are fairly fast but have low equilibrium constants [32]. However, an example of reactions of the type

$$A + B \rightarrow C + D.$$

under chromatographic conditions has been described [175]. One of the starting materials is then either continuously passed through the catalyst in the stream of the carrier gas or introduced as a pulse, mixed with other components. Probably in this case the starting materials are not separated in the reactor and therefore reaction between them is possible.

Roginskii and coworkers made a theoretical analysis of heterogeneous catalytic reactions of various orders under conditions of ideal linear chromatography and derived

equations for the rate constants and the activation energies for first-order reactions, which they used in the study of the dehydrogenation of cyclohexane to benzene on a number of catalysts [33]. They showed [176] that the rate constants for the reaction can be determined not only from the degree of conversion at various carrier gas flow rates but also from the shape of the product output curve obtained at a single carrier gas flow rate, on the assumption that under the experimental conditions the adsorption isotherm of the product on the catalyst is linear.

The use of radioisotopes and of an additional radiometric detector provides in this case too an effective means of determining the mechanism of the process when the latter is carried out under chromatographic conditions. For example, confirmation has been obtained of the absence of the reverse reaction in the dehydrogenation of cyclohexane on a platinum catalyst in an inert carrier gas [31] and in the dehydrogenation of butenes to divinyl under chromatographic conditions [177].

The results of the study of a catalytic process under chromatographic conditions provide additional information both about the process itself and about the state of the catalyst. The possible advantages of these conditions in industry have not so far been considered. The possibility that in some processes pulse conditions may prove effective cannot be excluded.

IV. GAS-CHROMATOGRAPHIC STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF CATALYSTS

In heterogeneous catalysis chemical processes are accompanied by adsorption. Therefore the study of the adsorption properties of catalysts constitutes a very important problem. The main characteristics of adsorbents are their structural properties (specific surface, porosity, i.e. quantities which are independent of the properties of the substances adsorbed) and their properties determined by the nature of the adsorbent–adsorbate system (adsorption energy, adsorption isotherm, and others).

Since in gas chromatography the retention time (volume) and the shape of the peak due to a given substance depend on the properties of the adsorbent and the substance adsorbed, it was natural to consider the reverse problem: to investigate on the basis of chromatographic data the properties of adsorbents and catalysts with the aim of reducing the time required for chromatographic investigations. It was found that, with certain assumptions, it is possible to establish a mathematical relation between the specific retention volume of a given substance and the specific surface of the catalyst [36] and between the shape of the chromatographic peak and the adsorption isotherm [178], while the temperature variation of the retention volume makes it possible to determine the heat of adsorption [39]. A chromatographic method for the determination of the activity of certain catalysts has also been described [37].

In most of the studies dealing with the determination of the surface area of adsorbents and catalysts by gas chromatography, use is made of the relation, derived by Wilson, between the form of the chromatographic curve and the form of the adsorption isotherm in the absence of complications associated with the kinetics of the adsorption and longitudinal diffusion (conditions of equilibrium chromatography) [35,179-181]. On the basis of chromatographic data, it is possible to obtain adsorption isotherms on catalysts at different temperatures and to determine the absolute specific surface of the catalyst. Either adsorption–desorption curves or display chromatograms are then employed.

However, more accurate results are given by Nelsen and Eggertsen's thermal desorption method [34,182,183], in which the conditions of equilibrium chromatography are not required, this being particularly important in the study of finely porous adsorbents and catalysts. This method constitutes the basis of gas-chromatographic sorption meters [184,185].

By using as adsorbates substances of different molecular size, it is possible to estimate the nature and distribution of the pores with respect to radius [186]. A method has also been described for the determination of the relative surface area, based on the determination of the specific retention volume V_g at low concentrations, which is proportional (within the limits of experimental error) to the specific surface S_g: [36,187-189]

$$S_g = AV_g \qquad (1)$$

where A is a proportionality coefficient, which depends on the nature of the adsorbent–adsorbate system and on temperature. Eqn. (1) has been tested on a large number of catalysts [36]. The method is recommended for the measurement of the variation of the catalyst surface during its operation and also for rapid estimates of the surface areas of adsorbents and catalysts of the same chemical type.

Kiselev and coworkers [190,191] suggested that the retention volume of a given substance, referred to unit area of the adsorbent, be used as a characteristic of adsorbent–adsorbate systems:

$$V_s = \frac{V_g}{S_g},$$

where V_s is independent of the adsorbent surface area and reflects mainly the properties per unit surface.

The gas-chromatographic method can also be used to investigate chemisorption. Adsorption isotherms and isochores have been obtained for hydrogen on a number of metals and the kinetics of its chemisorption have been studied [192]. Such data may be useful in the investigation of hydrogenation catalysts.

The gas-chromatographic method has also proved an effective means for the investigation of catalysts with acid properties. Thus the total number of acid centres and the strength of their acidity under conditions obtaining in the operation of the catalyst can be found from the amount of chemisorbed ammonia (or an organic base), which can be readily obtained from a frontal chromatogram [183,193]. The effect of surface acidity on the adsorption of hydrocarbons and on catalyst activity has also been investigated with the aid of gas chromatography [38,193,194].

Misono et al. [38] proposed a gas-chromatographic method for the simultaneous determination of the distribution of acid centres with respect to the strength of their acidity and catalytic activity under conditions obtaining in the operation of the catalyst. The method consists in the determination of the retention volume and the heat of adsorption of benzene (a weak base) on the catalyst at different surface coverages of the latter with pyridine (a strong base). From these data, it is possible to construct the curve representing the distribution of the acid regions with respect to the strength of their acidity in terms of the benzene heat of adsorption scale, assuming that pyridine blocks such regions, starting with the most acid ones. If instead of benzene a reactant is admitted to the catalyst, it is possible to investigate, on the basis of the reaction products corresponding to different degrees of poisoning of the acid

centres by pyridine, the activity and selectivity of the catalyst in relation to different types of reaction, depending on the acid strength.

The results obtained in the study of the distribution of acid centres with respect to their acid strength obtained by the above method have been confirmed qualitatively by an indicator method. The advantage of the chromatographic technique is that the determination of the acidity is performed under the conditions of the catalytic process itself. Furthermore, the colour of the catalysts, which interferes with indicator measurements, is without importance in the chromatographic method.

The application of gas chromatography in the determination of the heat of adsorption is based on the fact that, under conditions of ideal chromatography (when the isotherm is linear), the logarithm of the retention volume of the given substance is proportional (after certain necessary corrections) to the free energy of adsorption, and the heat of adsorption can be found from the slope of the linear plot of the logarithm of the adsorbate retention volume against the reciprocal of absolute temperature[39,195,199]. It is assumed that the effect of diffusion and of the finite rate of mass exchange is slight and may be neglected[199]. A chromatograph designed specially for the measurement of heats of adsorption has been described[200]. While it cannot replace the more reliable and detailed calorimetric technique, the chromatographic method permits rapid, simple, and fairly accurate determination of the heat of adsorption.

Comparison of the heats of adsorption determined by both methods shows good agreement in most cases. The discrepancy between the results is mainly due to the different surface coverages used in the two methods[39,198]. Since gas chromatography is highly sensitive, it permits the determination of the heat of adsorption at surface coverages so low that there is no interaction between the adsorbed molecules even when they are capable of association. On combining this method with some other, applicable to higher coverages (for example the calorimetric method), it is possible to determine the energy of association in the adsorption layer. The energy of the hydrogen bond between molecules of alcohols adsorbed on the surface of graphitised carbon blacks has been determined in this way[201,202].

The chromatographic method makes it possible to extend the range susceptible to investigation to temperatures of 300–500° and to measure the heat of adsorption under conditions close to those in a catalytic reaction. These advantages are lacking in the calorimetric method and in the method involving the calculation of isosteric heats from adsorption data, which are usually employed[197,199]

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PERCHLORYL FLUORIDE: PRODUCTION, PHYSICAL PROPERTIES, AND REACTIONS

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I. INTRODUCTION

The rapid development of investigations into the preparation and chemistry of perchloryl fluoride $FClO_3$† has made it available not only for study, but also for practical applications.

The marked difference between the exceptionally stable $FClO_3$ and the other unstable oxide fluorides of chlorine has made it of special interest. The high symmetry of its molecule and the great similarity in electronegativities of fluorine and the ClO_3 group explain the stability of perchloryl fluoride and its chemical behaviour as a two-centre electrophilic substance. It is still the only reagent for perchlorylation (introduction of the ClO_3 group) at carbon in organic compounds and at the same time it exhibits the properties of a selective fluorinating agent. The oxidative dimerisation and oxofluorination which can be effected with the aid of $FClO_3$ are reactions of independent interest. The fact that the perchloryl fluoride molecule is made up of atoms of the most electropositive elements determines its behaviour as a strong oxidant.

The available literature on the properties of this compound has been very inadequately surveyed. Brief reviews in Japanese[1] and Chinese[2] have been published, but these dealt with only a small part of the literature. A Russian review[3] which recently appeared was principally devoted to the selective fluorination of steroids.

In the present review we aim to cover as completely as possible the literature on the production, physical properties, and reactions of perchloryl fluoride in the period from 1950 to mid-1965.

II. PRODUCTION OF PERCHLORYL FLUORIDE

Perchloryl fluoride was first obtained by Engelbrecht and Atzwanger[4] in 1952 by the electrolysis of a saturated solution of sodium perchlorate in anhydrous hydrogen fluoride, with a current efficiency of 10%.

A year earlier, Bode and Klesper, who investigated the action of elemental fluorine on potassium chlorate, reported the production of a compound of composition $FClO_3$,[5] which in reality was a mixture of chloryl fluoride $FClO_2$, chlorine, and perchloryl fluoride[6,7]; the last can be isolated in yields of up to 45%.[8] The fluorination was carried out in the solid phase using fluorine diluted with nitrogen at temperatures up to 50°C. The use of efficient cooling (-25°C) and strict control of temperature in working with undiluted fluorine, supplied at a low rate, allowed the yield of $FClO_3$ to be increased to 60%.[9]

† Better written ClO_3F (Ed. of Translation).

In addition to perchloryl fluoride, several gaseous products are formed in the reaction of potassium chlorate with fluorine: Cl_2, $FClO_2$, O_2, Cl_2O_6, and FCl.[8,9] To free $FClO_3$ from impurities it is passed through alkaline solutions of reductants and then condensed at liquid oxygen temperature. This method seemed so effective (after the treatment the proportion of impurities did not exceed 1.5%) that it was used without significant changes in all subsequent work on the preparation of perchloryl fluoride.

Note that both methods (electrochemical and the fluorination of chlorates by fluorine) have several drawbacks: the need to work with special metal apparatus, the difficulty of temperature control in solid-phase fluorination, low yields, etc.

Replacement of elemental fluorine by other fluorinating agents (ClF_3, BrF_3, SbF_5) did not give positive results: the yield of perchloryl fluoride was too low, and the main reaction products with potassium chlorate were $FClO_2$ and Cl_2.[8] Only the use of perchlorates instead of chlorates led to the development of convenient methods of making $FClO_3$.

When potassium perchlorate is heated (70–120°) in an excess of antimony(V) fluoride, perchloryl fluoride is formed in 50% yield. Other metal perchlorates (sodium, barium, magnesium) or perchloric acid can be used in this reaction[10].

Of other reactions, that of perchlorates with fluorosulphonic acid has been studied in greatest detail[11-17]. This method of obtaining $FClO_3$, which was proposed in 1956 by Barth-Wehrenalp[11], is now evidently the simplest and most convenient. Solutions of potassium perchlorate in fluorosulphonic acid are heated at various temperatures. Liberation of perchloryl fluoride starts at 50°, the reaction goes to completion with the temperature gradually rising to 85° or 110°. The yields of perchloryl fluoride vary within the range 50–80%[11-13]. If necessary the fluorosulphonic acid can be regenerated for reuse[12]. The great convenience of the method is that the reaction can be carried out in the usual glass apparatus; moreover the initial substances are available and cheap.

Unfortunately the mechanism of the process has been little studied. The initial suggestion[11] that the compound $(ClO_2)_2S_3O_{10}$ was formed as an intermediate was disproved after a more critical consideration[15,16]. It is now thought more probable that there is an acid–base reaction, expressed by the equation:

$$3\,HSO_3F + KClO_4 \rightleftarrows ClO_3^+ + 3\,SO_3F^- + H_3O^+ + K^+,$$

and the formation of $FClO_3$ is considered to be the result of the thermal decomposition of this equilibrium mixture[15].

With the aim of increasing the yield of perchloryl fluoride in the reaction of potassium perchlorate with fluorosulphonic acid the influence of various fluorine-containing additions was studied: BF_3, HF, SbF_3, and other metal fluorides[17]. Thus, the addition of 5–25 parts SbF_3 per 100 parts fluorosulphonic acid increases the yield of $FClO_3$ to 90% and over. Addition of BF_3 and HF also increases the yield to 85%. Unfortunately, the introduction of these has a bad effect on other aspects of the reaction: SbF_3 hinders the regeneration of fluorosulphonic acid, and BF_3 and HF require pressure for carrying out the reaction. Zinc, aluminium, silver, and lead fluorides, on the other hand, decrease the yield of perchloryl fluoride[17].

The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulphonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature (100–135°) the reaction time is 1–10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over, air and carbon dioxide being present as trace impurities[18,19].

III. PHYSICOCHEMICAL PROPERTIES OF PERCHLORYL FLUORIDE

The physical and physicochemical properties of perchloryl fluoride have now been studied rather fully (see Table 1).

Under ordinary conditions perchloryl fluoride is a colourless gas with a characteristic sweetish odour. On cooling to -46.8° it condenses to a colourless liquid, which solidifies at -147.75°.

Unlike other compounds of fluorine with oxygen and chlorine (F_2O, $FClO_2$, $FClO_4$, ClF_3, etc.), perchloryl fluoride exhibits exceptional thermal and hydrolytic stability. Dry perchloryl fluoride is almost stable on heating to 500°[20] and is not hydrolysed in the slightest by water even on heating to 250–300°.[8] Perchloryl fluoride does not explode on detonation, but it forms explosive mixtures with certain organic substances[20], which must be taken into account in working with it.

Addition of an inhibitor is not needed for storing $FClO_3$ in either the liquid or the gaseous states. Dry perchloryl fluoride does not corrode most common metals[20]. It does not react with stainless steel, copper, or aluminium[21,22]; of organic materials, Kel-F oil — poly(chlorotrifluoroethylene)[22] — and ethylene–propylene rubber[23] are chemically rather stable towards it. Moist perchloryl fluoride reacts appreciably with vacuum grease and with mercury[24].

TABLE 1.

Physicochemical properties of perchloryl fluoride	Reference
Boiling point −46.68°C	24
Melting point −147.75°C	24
Density of liquid at 20°C 1.434 g ml^{-1} *	27
Critical parameters:	
temperature 95.17°C	27
pressure 53.0 atm	27
density 0.637 g ml^{-1}	8
molar volume 161 cm^3	8
Trouton's constant 21.97	8
Heat of vaporisation	
at boiling point 4.6 kcal $mole^{-1}$	24,27
at 25°C 3.5 kcal $mole^{-1}$	29
Viscosity of liquid:	
at −80°C 0.62 cP	29
at 0°C 0.219 cP	
at +60°C 0.139 cP	
Heat capacity of the liquid at 50°C 0.29 cal g^{-1} deg^{-1}	29
Density of the solid at −190°C 2.19 g cm^{-3}	31
Heat of fusion 916 cal $mole^{-1}$	24
Surface tension at −55.6° 21.3 dyn cm^{-1}	28
Ratio C_p/C_v at 24°C 1.12 ± 0.01	32
Entropy at 25° 66.51 e.u.	24

* It appears that the authors have used an equation for the liquid density as a function of temperature obtained in the range 131°K to 234°K[27] and has used this to give the figure quoted for density at 20°C! (Ed. of Translation).

Perchloryl fluoride is sparingly soluble in water, rather more soluble in organic solvents. Under ordinary conditions (25°, 760 mmHg) its solubility varies within the range 1.5–5.5 g litre^{-1}. The highest solubility is in dioxan, nitrobenzene, and dimethyl formamide [1,25,26].

Empirical equations have been obtained for the temperature dependence of vapour pressure [8,24,27], the density of the liquid [8,27], and the viscosity of the liquid [28]. Detailed information has been published on the heat capacity of liquid perchloryl fluoride at various temperatures [24,29,30], its surface tension [28], and viscosity [28,29].

Structure and Spectra

A compound of composition $FClO_3$ can have one of two structures:



(A) (B)

On the basis of the vibrational spectra, perchloryl fluoride was ascribed structure (B), having the chlorine as central atom and symmetry of type C_{3v}. [33,34] In fact, on comparing structures (A) and (B), the first should have the structure of a triangular pyramid and the second a tetrahedron with the chlorine atom at the centre. Structure (A) could not have symmetry of a type higher than C_s, whereas structure (B) corresponds to a symmetry of type C_{3v}. Accordingly, structure (A) would correspond to the presence of nine main bands active in the infrared region, and structure (B) to six bands. In the observed spectrum of $FClO_3$ there are only six main frequencies (see Table 2), which supports structure (B). The absence of a microwave spectrum for perchloryl fluoride is also considered as confirmation of the C_{3v} model [35].

The infrared spectrum of $FClO_3$ has also appeared in other papers [8,36]. The assignment of the frequencies, made on the basis of a comparison with the spectra of ClO_4^- and FCl, [33] was confirmed by investigation of the Raman spectra [37,38] (see Table 2) and of the high-resolution infrared spectrum in the 525–625 cm^{-1} region [34].

Some correlations with the infrared spectra of perchloryl fluoride have also been made. Thus, Sharp [39] notes a significant similarity in the infrared spectra of $FClO_3$ and FSO_3^-, which is isoelectronic with it; Robinson [40] found a linear relation between the frequencies of the symmetric and asymmetric stretching vibrations of the $-PO_2$ and $-ClO_2$ groups which is also suitable for many oxygen ligands.

TABLE 2. Vibrational spectra of perchloryl fluoride*.

Raman spectrum (Ref.37)	Infrared spectrum (Ref.33)	Assignment of frequencies
410 v.s.	405	ν_6 (e) rocking
549 s.	549	ν_3 (a_1) deformation ClO_3
587 m.	589	ν_5 (e) deformation ClO_3
695—724 m.	704	ν_2 (a_1) stretching $^{37}Cl-F$
	714	ν_2 (a_1) stretching $^{35}Cl-F$
1061 v.s.	1061	ν_1 (a_1) stretching Cl—O
1312 w.	1315	ν_4 (e) stretching Cl—O

* s strong; vs very strong; m medium; w weak.

The values of the frequencies here depend regularly on the electronegativity of the groups connected to the central atom.

The dipole moment of perchloryl fluoride is very low [35]; its accurate value of 0.023 ± 0.003 D was determined by using specially sensitive apparatus [41].

From measurements of the vapour pressure, heats of fusion and vaporisation, and the phase transformation temperatures, the entropy of perchloryl fluoride as an ideal gas at the boiling point has been calculated [24] to be 60.17 e.u. From the table of thermodynamic properties [42] this quantity was found to be 62.59 e.u. (interpolation). For a crystal with disordered arrangement of the F and O atoms at 0°K the difference in these quantities should be $R \ln 4 = 2.75$ e.u. The fact that the observed difference is slightly less than this value shows that there is a high degree of disorder in the arrangement of the fluorine and oxygen atoms in the perchloryl fluoride crystal [24].

Tallman and coworkers [31,43] give X-ray diffraction data and the density of crystalline perchloryl fluoride at liquid air temperature. From these data the authors assume that crystalline perchloryl fluoride has a tetragonal cell ($a = b = 7.66$ Å, $c = 5.31$ Å). The ^{19}F-NMR spectra of perchloryl fluoride have been discussed [44–46]. According to the interpretations in References 44 and 46 the observed spectra are the sum of $F^{35}ClO_3$ and $F^{37}ClO_3$ spectra, in each of which there is spin–spin interaction of the fluorine nucleus with the nucleus of the corresponding Cl isotope (both isotopes have spin $I = \frac{3}{2}$). The F–Cl spin–spin interaction which is observed extremely rarely in spectra here becomes observable, apparently owing to the low rate of relaxation of the chlorine nucleus, which is in turn due to the highly symmetrical environment of the chlorine atom (that is, the anomalously low constant of the quadrupole interaction of the chlorine nuclei). The very high chemical shift (320 p.p.m. to lower fields relative to CF_3CO_2H lines) shows the extremely low negative charge on the fluorine, in other words, the high degree of covalency of the F–Cl bond in the $FClO_3$ molecule. The fact that the electronegativities of fluorine and the ClO_3 group are close to one another is also confirmed by the absence of a dipole moment from $FClO_3$. [41]

The mass spectrum of perchloryl fluoride has been studied [47–49]. The potentials for the appearance and the relative intensities of the negative [47,49] and positive [49] ions in the mass spectrum have been determined. On the basis of these potentials hypothetical values have been advanced for the ionisation energies of the radicals obtained in the breakdown of the $FClO_3$ molecule, and the heat of formation of perchloryl fluoride has been estimated to be -5.3 ± 4 kcal × × mole^{-1} (in good agreement with the -5.12 ± 0.68 kcal × × mole^{-1} from another study [50]) and the dissociation energies of the bonds to be $D_{(O_3Cl-F)} = 60$ kcal mole^{-1} and $D_{av(Cl-O)} = 57$ kcal mole^{-1}. [49]

IV. REACTIONS OF PERCHLORYL FLUORIDE

As noted above, perchloryl fluoride exhibits high thermal stability and considerable stability to hydrolysis. Appreciable thermal decomposition of perchloryl fluoride is observed only at temperatures of ~500°C. Gatti and coworkers [51,52] studied the kinetics of thermal decomposition of perchloryl fluoride at 470–500°C over a wide pressure interval (5–1000 mmHg) by the equation

$$2FClO_3 \rightarrow 2ClF + 3O_2.$$

They found that the reaction is unimolecular and completely homogeneous (in quartz); the activation energy is 58.4 ± 2 kcal mole^{-1}.[52] The application of a dimensionless molecular transfer equation, based on similarity theory, to chemical kinetics, in particular for the example of thermal decomposition of perchloryl fluoride, allowed the main kinetic characteristics of the process (rate and activation energy) to be obtained without employing any assumptions about the mechanism[53].

1. REACTIONS WITH INORGANIC COMPOUNDS

Perchloryl fluoride does not react with dilute aqueous solutions of alkalis or thiosulphate, nor with solid alkalis[8,13].

Even at 250–300° the hydrolysis of $FClO_3$ is very slow. Quantitative hydrolysis is brought about by concentrated alkali solutions at the same temperature, according to the equation:

$$FClO_3 + 2\,NaOH \rightarrow NaClO_4 + NaF + H_2O.$$

However, in an alcoholic solution of potassium hydroxide perchloryl fluoride is readily split at 25°C with the formation of a precipitate of $KClO_4$, and KF is left in solution. This reaction can be used for the quantitative determination of $FClO_3$.[1]

The reaction of $FClO_3$ with sodium and potassium starts only at ~300°C, although it proceeds rather vigorously[8].

All these results led initially to perchloryl fluoride's being considered a chemically inert substance but, as appeared subsequently, this does not correspond with reality. Perchloryl fluoride is capable of reacting vigorously with several inorganic and organic compounds at moderate temperatures and even on cooling below 0°C.

Perchloryl fluoride reacts rather easily with liquid ammonia or its aqueous solutions[8,54] by the equation:

$$FClO_3 + 3\,NH_3 \rightarrow NH_4F + NH_4NHClO_3.$$

The reaction takes place quantitatively in a few hours. Sodium amide greatly accelerates the reaction in liquid ammonia. From the ammonium salt perchloryl amide, which could not be isolated pure, the silver, caesium, and potassium salts have been obtained: $AgNHClO_3$, $CsNHClO_3$, Cs_2NClO_3, $KNHClO_3$, K_2NClO_3, which are derivatives of the unstable amide of perchloric acid, $H_2N{-}ClO_3$. These salts, especially in the dry form, are sensitive to impact, friction, and the action of a flame.

Perchloryl fluoride oxidises potassium iodide. The reaction proceeds quantitatively on shaking for 4–5 h a solution of KI in 0.1 *N* acid with perchloryl fluoride[8]:

$$FClO_3 + 8\,I^- + 6\,H^+ \rightarrow Cl^- + F^- + 4\,I_2 + 3\,H_2O.$$

In his review Nakanishi[1], in referring to published data[55], states that oxidations involving $FClO_3$ depend to a considerable extent on the reaction temperature, the pH of the medium, and the concentration of the reagents. At high temperatures many reactions proceed explosively. For example, a mixture of $FClO_3$ and H_2S in certain proportions explodes at 150°. With a dilute mixture the rate of reaction at this temperature is low and the reaction is:

$$3\,FClO_3 + 4\,H_2S \rightarrow 4\,SO_2 + 3\,HF + 3\,HCl + H_2O.$$

Reaction with hydrogen chloride in the gas phase at 200–300° proceeds with the formation of chlorine by the equation:

$$FClO_3 + 7\,HCl \rightarrow HF + 4\,Cl_2 + 3\,H_2O.$$

2. REACTIONS WITH ORGANIC COMPOUNDS

In reactions with organic compounds $FClO_3$ behaves as either an oxidant or a two-centre electrophile which, depending upon the conditions, can be used for the introduction of either fluorine or the ClO_3 group.

Fluorination

The reaction of perchloryl fluoride which has been studied best is the fluorination of organic compounds at a carbon having a mobile hydrogen atom. These include compounds with a methylene or methine group activated by one or more electronegative groupings (ketone, alkoxycarbonyl, aldehyde, nitrile, etc.). A necessary condition for the fluorination is the presence of an equimolar amount of a base (usually an alkali metal alkoxide) or the introduction into the reaction of a previously prepared metal derivative of the compound being fluorinated.

Carbonyl compounds. Inman and coworkers[56,57] effected the first fluorinations of compounds with an active methylene group by the action of perchloryl fluoride. They found that ethyl and phenyl malonates react smoothly with perchloryl fluoride in the presence of bases, giving the corresponding monofluoro-substituted esters with yields of over 70%:

$$RCH(COOC_2H_5)_2 \xrightarrow{FClO_3} RCF(COOC_2H_5)_2.$$

The fluorination of malonic esters proper does not stop at the stage of the monofluoro-derivative but leads to the exclusive formation of the difluoromalonate even when there is insufficient base‡. The authors' explanation for this is that the monofluoromalonate ester, which is evidently a stronger acid§ than malonic, undergoes the fluorination more rapidly.

‡ After this review had been written there appeared a paper by Gershon and coworkers[124] describing a more detailed investigation of the action of perchloryl fluoride on malonic ester. It was found that in this reaction in addition to the difluoromalonate there are several other products, including the monofluoromalonate. The qualitative and quantitative composition of the mixture depends on the solvent and the ratio of the reactants.

§ We do not think that this conclusion of the authors is sufficiently well founded. It was recently established[125,126], for fluoronitroalkanes, that the introduction of a fluorine atom in the α position to an electron-acceptor substituent (the nitro-group) does not increase, but, on the contrary, greatly lowers the acidity of the compound. In accordance with this, fluoromalonic ester should be a weaker, not a stronger, acid than malonic ester. On the other hand the ease of fluorination is evidently determined more by the nucleophilic nature of the compound being fluorinated than by its acidity.

Perchloryl fluoride reacts readily with β-keto-esters [57-59], α-substituted keto-esters giving the monofluoro-derivatives [58,59], but acetacetic ester giving the difluoro-derivative exclusively [57]:

$$CH_3COCHCOOR' \xrightarrow{FClO_3} CH_3COCFCOOR'$$
$$\quad\quad R \quad\quad\quad\quad\quad\quad R$$
$$CH_3COCH_2COOC_2H_5 \xrightarrow{FClO_3} CH_3COCF_2COOC_2H_5$$

A side-reaction here is the removal of the acetyl group, which is facilitated by an excess of the base and raising the temperature. Thus, in the fluorination of the ethyl ester of 2-acetyl-5-methylhex-4-enoic acid two compounds were isolated: the expected fluorination product (I) and its diacetylated analogue (II) [58]:

$$(CH_3)_2C=CHCH_2\underset{\underset{COCH_3}{|}}{CH}COOC_2H_5 \xrightarrow{FClO_3} (CH_3)_2C=CHCH_2\underset{\underset{COCH_3}{|}}{CF}COOC_2H_5 + (CH_3)_2C=CHCH_2CFHCOOC_2H_5$$
(I) 65% (II) 10%

The acetyl group is even more readily detached from fluorinated acetyl diesters. Thus, in the presence of bases fluorination of esters of type (II) leads to the formation of a deacetylated compound as the main product — a monofluoromalonic ester — and only a little of fluorination product (IV) [59]:

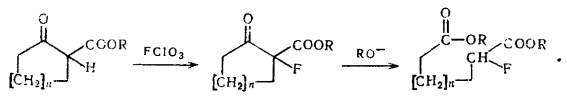
$$R'CCH(COOC_2H_5)_2 \xrightarrow{FClO_3} R'CCF(COOC_2H_5)_2 \xrightarrow{ROH,RO^-} R'COOR + CHF(COOC_2H_5)_2$$
(III) (IV)

In the fluorination of esters of tricarboxylic acids an ethyloxalyl group can be removed [60,61].

The property of the α-fluoro-α-alkyl-β-keto-esters to lose an acetyl group under the action of bases or an alkoxycarbonyl group in OH-catalysed hydrolysis was used for a directed synthesis of several esters of α-fluorocarboxylic acids [59] and α-fluorinated ketones [58]:

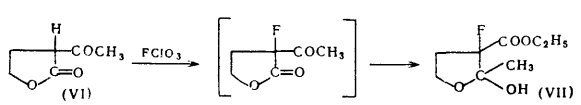
$$RCFCOCH_3 \quad (COOR') \xrightarrow{RO^-} RCFHCOOR' \quad (OH^-) \rightarrow RCFHCOCH_3$$

Cyclic β-keto-esters react with perchloryl fluoride like the acyclic esters [62], but not all the fluoro-compounds which are obtained (V) are stable:

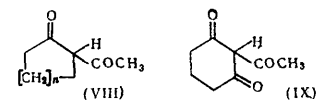

(V)

Thus the fluorination product (V; n = 1) could not be isolated, as it underwent a series of changes, leading to ring opening. The most stable fluorination products were compounds with larger rings (V; n = 2, 3) or bicyclic systems. Under the action of alkaline agents compounds of type (V) are readily hydrolysed and decarboxylated, forming cyclic α-fluoroketones [62,63].

On reaction with perchloryl fluoride, lactones of type (VI) also give unstable fluoro-derivatives which undergo a series of transformations under the conditions of the reaction [59,64]. Thus, the final result of the fluorination of lactone (VI) was the formation of (VII) [59]:

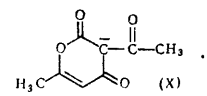

(VI) (VII)

Cyclic β-diketones (VIII) and triketones (IX) also react with $FClO_3$; the regularity in the formation of fluorination products for them is the same as for cyclic β-keto-esters — ring opening, deacetylation [62]:

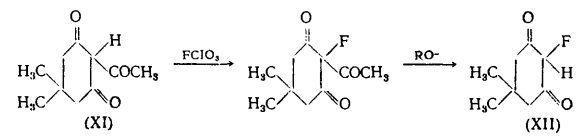

(VIII) (IX)

The less nucleophilic nature of the anions of tricarbonyl compounds (in comparison with dicarbonyl compounds) leads to a decrease in the reactivity towards perchloryl fluoride, and the reaction is slow.

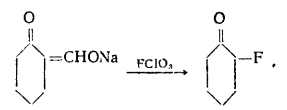
Anions which are still more resonance-stabilised such as (X), generally do not react with perchloryl fluoride [62].


(X)

In the example of tricarbonyl compounds reacting with $FClO_3$ mention must be made of the side-reaction, which can occur in the fluorination of other compounds. When the reaction leads to the formation of compound (XII), which is a stronger acid than the original compound (XI), the former can displace the latter from its salts. Then the compound being fluorinated (XI) is partly recovered unchanged, which leads to a fall in the yield of the desired reaction product:

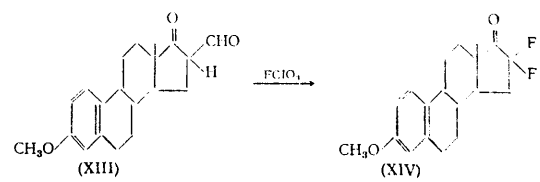

(XI) (XII)

α-Formylated cyclic ketones behave analogously to α-acetylketones in reaction with perchloryl fluoride: the fluorination is accompanied by loss of the formyl group and sometimes the difluoro-derivative is formed. Fluorination of sodium 2-oxocyclohexylidenemethoxide leads to the formation of 2-fluorocyclohexanone in 40% yield [65]:



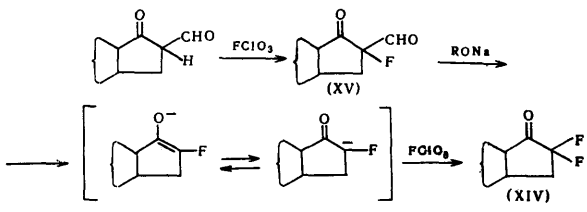
Dipole moment measurements have established the equatorial conformation of the fluorine in the 2-fluorocyclohexanone obtained. This compound serves as a standard for finding the conformation of the α-fluoroketones of the steroidal series.

The fluorination of the α-formylated cyclic ketones has been used successfully to obtain fluorinated analogues of certain steroids¶. Thus, the 3-methyl ether of 16-formyl-oestrone (XIII) reacts with $FClO_3$ in t-butyl alcohol to give at once the 3-methyl ester of 16,16-difluoro-oestrone (XIV) in the presence of a large excess of sodium butoxide [67]:


(XIII) (XIV)

¶ Methods of obtaining fluorosteroids have been reviewed in detail. [66]

The authors assume that the monofluoroformyl derivative (XV) is formed as an intermediate, which subsequently reacts with the base and perchloryl fluoride to give the $\alpha\alpha$-difluoroketone (XIV):

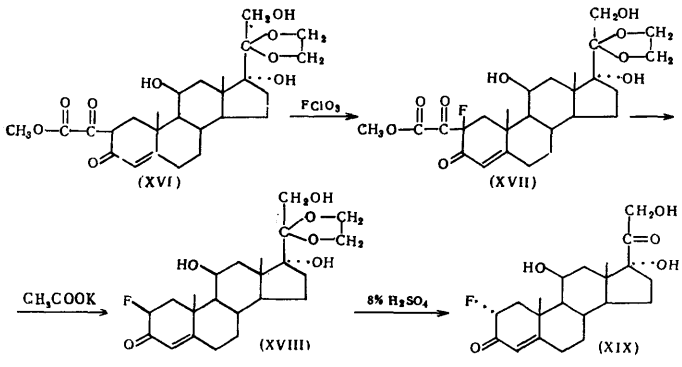


Proof of the proposed scheme was given by the isolation of the monofluoroketone (XV) corresponding to the first stage of the reaction[68].

Monofluoroketones of the androstane series were obtained by an analogous reaction in benzene; the 2-formyl--2-fluorosteroids formed on fluorination were treated with a base to remove the formyl group. For example: 2-fluorotestosterone, 2α-fluoro-17β-hydroxyandrostan--3-one, etc. were obtained in this way[69].

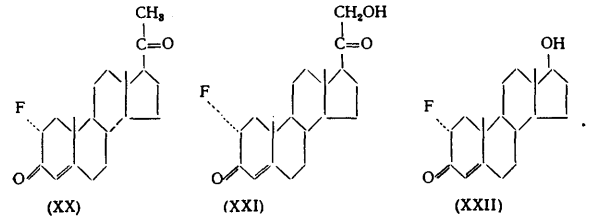
The introduction of fluorine into positions 6α 9α, and 12α of hydrocortisone leads to highly active glucocorticoids. The reaction of $FClO_3$ with the sodium salts of the enol forms of β-dicarbonyl compounds is very convenient for obtaining fluorinated steroidal hormones. This method evidently allows fluorine to be introduced into any methylene or methyl group of the steroid capable of alkylation with the formation of a β-dicarbonyl system. In turn the acylation is conveniently effected by the introduction of an alkoxalyl group[70,71] which is readily detached after fluorination.

For the synthesis of 2α-fluorohydrocortisone, 20-ethyleneketalhydrocortisone was treated with methyl oxalate and sodium methoxide in benzene. The ethyleneketal was taken to prevent methoxalylation at position 21. The 2-methoxalylhydrocortisone-20-ethyleneketal (XVI) which was obtained reacted with perchloryl fluoride[72,73]:



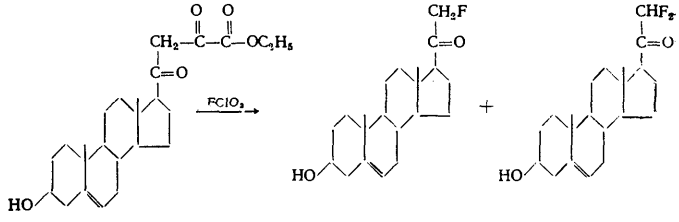
After removal of the methoxalyl group from (XVII) the substance (XVIII) was obtained in 43% yield. The yield of the desired 2α-fluorohydrocortisone (XIX) from (XVIII) was 73%.

2α-fluoroprogesterone (XX) was obtained analogously (44% yield calculated on the initial ethyleneketal), 2α-fluorodeoxycorticosterone (XXI) (25%), and 2α-fluorotestosterone (XXII) (20%)[72]:



A series of fluoro-substituted steroids containing fluorine in positions 2 and 21 has been obtained by the reaction of $FClO_3$ with alkoxalylated steroids[25,72-76]. Most authors consider the conformation of the 2-fluoro-3-keto-derivatives of steroids which are obtained to be equatorial (2α) from measurements of the dipole moments and by analogy of the optical rotatory dispersion curves with those for other halogeno-substituted compounds for which the conformation has been established[65,72,74,78].

Both monofluoro- and difluoro-derivatives were obtained by the fluorination of the 21-ethoxylalyl derivatives of 20-keto-steroids[72]:



An interesting example of fluorination by perchloryl fluoride has been described[77]. It was shown that steroids with the $-\overset{\overset{O}{\|}}{C}-CF_2H$ group are capable of being fluorinated by perchloryl fluoride in the presence of bases, giving a trifluoro-derivative with the $-\overset{\overset{O}{\|}}{C}-CF_3$ group.

Fluorination of tetracyclines with perchloryl fluoride has also been described[79].

Nitriles and nitro-compounds. Compounds with a methylene group activated not only by carbonyl groups but also by other electronegative substituents (the nitrile group and the nitro-group) are fluorinated by perchloryl fluoride.

Substituted malonodinitriles[80] and phenylacetonitriles[81] give fluorinated products with $FClO_3$ in the presence of bases. It has been proposed to use as bases the alkali metals, and their hydroxides, hydrides, amides, and alkoxides[81]:

$$RC(CN)_2H \xrightarrow{FClO_3} RC(CN)_2F.$$

The sodium salts of secondary nitro-compounds (2-nitropropane, 2-nitrobutane, and nitrocyclohexane) are fluorinated by perchloryl fluoride in methanol, forming a fluoronitro-compound in 36-42% yield — Eqn. (1). The fluorination is accompanied by side-reactions: by oxidation and by oxidative dimerisation, as a result of which ketones — Eqn. (2) — and vicinal dinitro-compounds — Eqn. (3) — are formed[82]:

$$R_2C{=}NO_2^- + FClO_3 \rightarrow R_2CFNO_2 + ClO_3^- \quad (1)$$

$$R_2C{=}NO_2^- + FClO_3 \rightarrow R_2C{=}O + [HNO_2] + HClO_3 + F^- \quad (2)$$

$$2\,R_2C{=}NO_2^- + FClO_3 \rightarrow \underset{\displaystyle NO_2\ \ NO_2}{R_2C{-}CR_2} + F^- + ClO_3 \quad (3)$$

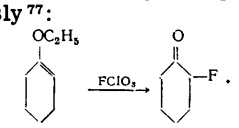
In the fluorination of primary nitro-compounds appreciable quantities of fluoronitroalkanes (3–5%) could not be obtained; mainly oxidation products are formed here — aldehydes (32–55%). Salts of such nitro-compounds as nitromalonic ester, α-nitro-α-phenyl acetophenone, etc., which have other electronegative substituents in the α position to the nitro-group are converted into the corresponding α-fluoronitro-compounds in high yields (80%)[83].

Oxidative dimerisation, which is observed as a side-reaction in the fluorination of nitroalkanes, is sometimes the main reaction. Thus, in an attempt to fluorinate acylamidomalonates with perchloryl fluoride in the presence of sodium ethoxide oxidative dimerisation products were obtained exclusively[84]:

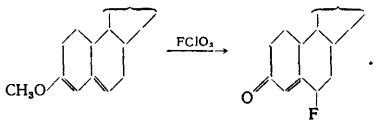
$$2\,RNH{-}CH(COOC_2H_5)_2 \xrightarrow{FClO_3} RNH{-}C(COOC_2H_5)_2{-}C(COOC_2H_5)_2{-}NHR$$

where R = HCO, CH_3CO.

Ethers of enols readily react with perchloryl fluoride in pyridine, forming α-fluoro-ketones in high yields. Thus 2-fluorocyclohexanone was obtained from 1-ethoxycyclohexene; the reaction with steroids having the same structural fragment — an ethoxy-group at a double bond — proceeds analogously[77]:



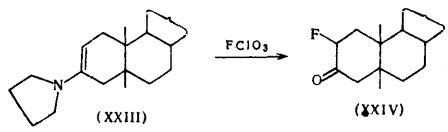
In the presence of two conjugated double bonds the fluorine enters position 6 of the steroid nucleus[77,85]:



Esters of enols (for example, acetates) react like ethers; the reaction takes place in an inert organic solvent, on adding weakly basic nucleophilic agents (water, pyridine)[86,87]. The reactivity of enol acetates with two conjugated double bonds is higher than with one double bond[88]; the latter react much more slowly[89,90].

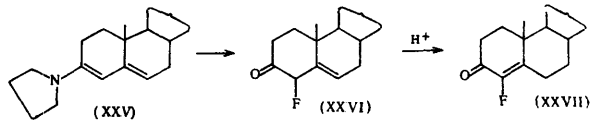
Enamines and enamides. The replacement of oxygen by nitrogen in steroid derivatives, that is, the use of enamides (acetylated enamines) instead of enol acetates considerably facilitates the fluorination. 3β-acetoxy-17-acetaminoandrosta-5,16-diene reacts with $FClO_3$ in pyridine at room temperature within 3 min, the yield of 3β-acetoxy-16α-fluoroandrost-5-en-17-one reaching 70% (against 45% after 20 h from the corresponding enol acetate)[90,91]. A sharp rise in reactivity of enamides compared with enol acetates agrees with the greater ability of the nitrogen atom to give electrons to a double bond, which should facilitate reaction with the electrophilic fluoride of the perchloryl fluoride[90,91].

Enamines are rather reactive in relation to $FClO_3$ but often give a mixture of different reaction products in ratios which depend on the fluorination conditions. Pyrrolidylenamine of cholestan-3-one (XXIII) gives 2α-fluorocholestan-3-one (XXIV) in 72% yield after passing $FClO_3$ into a benzene solution of (XXIII) for 30 s:[92]



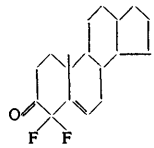
(XXIII) (XXIV)

Pyrrolidylenamines of steroids with two conjugated double bonds (XXV) in methanol and dimethylformamide react with $FClO_3$ to form monofluoro-substituted compounds of general formula (XXVI), the isomerisation of which in strongly acid medium leads to (XXVII)[93,94]:



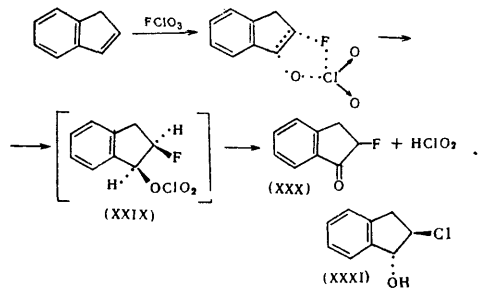
(XXV) (XXVI) (XXVII)

In ether enamines of type (XXV) give mainly 4,4-difluoro-3-keto-Δ^5-steroids (XXVIII)[95,96]:



(XXVIII)

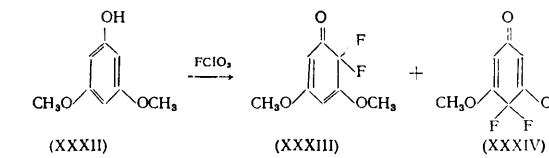
Oxofluorination. Compounds having a cyclic double bond conjugated with an aromatic nucleus, are capable of entering with perchloryl fluoride into the reaction termed oxofluorination, the final result of which is the formation of α-fluoroketones. For example, indene reacts in this way. In this reaction $FClO_3$ acts as a two-centre electrophile which attacks the 2–3 double bond of indene. As a result of this, according to the authors' hypothesis[97], a *cis*-fluoro-chlorate (XXIX) is formed as an intermediate, which is converted into the final α-fluoro-ketone (XXX) by loss of the acid $HClO_2$. This acid apparently takes part in the formation of the *trans*-2-chloroindanol (XXXI) which is isolated from the mixture in considerable quantity:



(XXIX) (XXX) (XXXI)

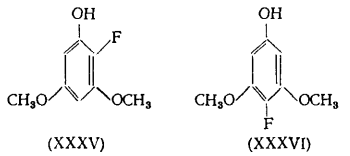
The products of oxofluorination are also formed by the action of perchloryl fluoride on the ethers of enols and enamines, as already mentioned above.

Phenols react with $FClO_3$, forming products of *C*-fluorination in which the fluorine usually enters the *ortho*- and *para*-positions. The molecule acquires a quinoidal structure. When perchloryl fluoride acts on 3,5-dimethoxyphenol (XXXII) in pyridine or dimethylformamide a mixture of two isomeric difluoro-compounds (XXXIII) and (XXXIV) is formed:



(XXXII) (XXXIII) (XXXIV)

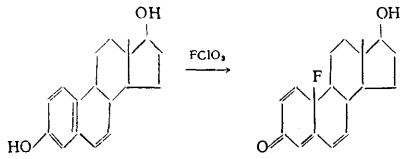
Paper chromatography of the reaction mixture allows the fluorophenols (XXXV) and (XXXVI) to be detected; they may be precursors of the final compounds (XXXIII) and (XXXIV) respectively:



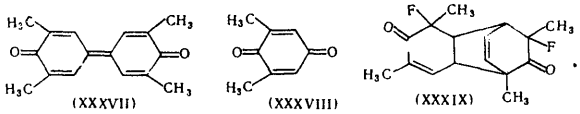
(XXXV) (XXXVI)

Reactions with 2- and 4-chloro-3,5-dimethoxyphenols give predominantly *gem*-chlorofluorodienones, the reduction of which with zinc in acetic acid leads to fluorophenols [98,99].

10β-fluorinated steroids are formed by the action of $FClO_3$ on steroidal phenols. In dimethylformamide the yields are higher than in dioxan [100,101]:

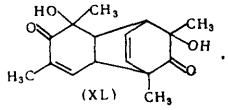


The reaction of perchloryl fluoride with phenols was studied in greater detail for 2,6-dimethylphenol [102]. As a result of the reaction of sodium 2,6-dimethylphenate a mixture of products was obtained, the composition of which depended on the solvent used. In media of low dielectric strength (pentane, dioxan, toluene) quinones (XXXVII), (XXXVIII), and a fluorination product in the form of a dimer (XXXIX) are formed:



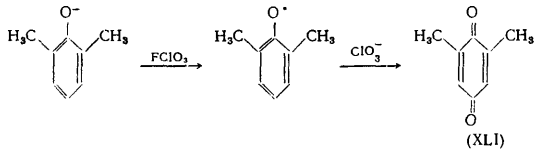
(XXXVII) (XXXVIII) (XXXIX)

In polar solvents (ethanol, dimethylformamide) instead of the dimer (XXXIX) a dimer of analogous structure (XL) is obtained:



(XL)

The authors explain the formation of quinones by the oxidation of the phenate anion to a radical and its subsequent conversion:



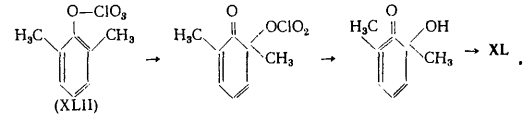
(XLI)

2,6-dimethylphenol itself in toluene does not react with perchloryl fluoride; in dimethyl formamide the reaction is very slow and a mixture of dimethylquinone (XLI) and 2,6-dimethyl-4-chlorophenol is formed. The formation of the latter can be explained by the action on 2,6-dimethylformamide of hypochlorous acid, which in turn is formed at the end of a sequence of redox changes:

$$FClO_3 \rightarrow ClO_3 \rightarrow HClO_2 \rightarrow OClH.$$

The definite influence of the medium on the formation of dimers (XXXIX) and (XL) prompted the authors [102] to suggest that these compounds are the products of the attack of a two-centre nucleophile — dimethylphenate — on perchloryl fluoride, which plays the part of a two-centre electrophile.

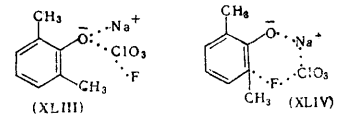
As a result of the attack by oxygen of the phenate ion on the chlorine of the perchloryl fluoride and subsequent intramolecular oxidative disproportionation of compound (XLII), the dimer (XL) is formed:



(XLII)

Were the nucleophilic centre the *ortho*-carbon atom of the phenate ion, then its attack by fluorine would lead finally to the dimer (XXXIX). The reaction of perchloryl fluoride at the carbon or oxygen of the phenate can be compared with the known *O*- or *C*-alkylation of phenates.

The transition state can be either (XLIII) or (XLIV):



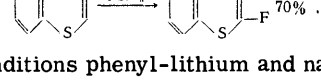
(XLIII) (XLIV)

The greater solvation of the cation favours the transition state (XLIII) which leads to the intermediate formation of the ester of perchloric acid (XLII) and then to the dimer (XL). Qualitatively similar results are observed in the alkylation in polar media, when, in accordance with the Ingold hypothesis, the phenate anion reacts at the oxygen and the ion pair at the carbon [103]. Here the more strongly solvating medium facilitates a shift in the equilibrium to the side of an increase in the number of ions (including the phenate anion), which leads, finally, to an increase in the yield of the dimer (XL).

On the other hand the quasicyclic structure of the transition state (XLIV) favours the loss of $NaClO_3$ owing to the electrostatic attraction between the Na^+ group and the ClO_3 group. The gain in energy of the C–F bond compared with F–Cl is also the driving force of the process.

The fact that carbanions usually react with perchloryl fluoride at the fluorine but heteroatomic anions (and amines) at the chlorine, is explained by the authors in the following way: *C*-fluorination is energetically quite a favourable process, whereas the low polarisability (in comparison with the mesomeric carbanions) of the heteroatomic anion and the high electron density at the hetero-atom leads to the repulsion of the *p*-orbital of fluorine and of the hetero-atom (nitrogen or oxygen) [102].

As yet the only example of the fluorination of heterocyclic compounds has been described by Schuetz and coworkers [104]. It was shown that in the presence of butyl-lithium thiophen and some of its derivatives are fluorinated by perchloryl fluoride in position 2:



Under these conditions phenyl-lithium and naphthyl-lithium give an extremely small quantity of fluoro-derivatives. With phenyl-lithium perchlorylbenzene could be isolated from the products of the reaction.

Oxidative fluorination. An interesting, but little studied reaction of $FClO_3$ is that with oximes. Perchloryl fluoride in pyridine is capable not only of fluorinating oximes at carbon, but also of simultaneously oxidising the oxime group to a nitro-group. Since, however, very few substances have been studied it is therefore uncertain how general this reaction is (so-called oxidative fluorination).

The dimethyl ester of oximinomalonic acid forms with perchloryl fluoride in dimethylformamide an oxidative fluorination product in 70% yield:

$$(CH_3OOC)_2C{=}NOK \xrightarrow{FClO_3} (CH_3OOC)_2C\begin{matrix}NO_2\\F\end{matrix}.$$

In the reaction potassium chlorate and chloride are formed. It is interesting that chloronitromalonic ester was isolated as a side-product, the quantity of which rose as the chloride ion accumulated[83]. In this respect the reaction differs from fluorination at an "active methylene" group, which is not sensitive to the presence of foreign ions[57].

The reaction could not be extended to other oximes, for example, the ethyl ester of α-oximino-β-ketobutyric acid† and the ethyl ester of oximinocyanoacetic acid. Some oximes under the action of $FClO_3$ undergo a Beckmann rearrangement of the second kind. Thus, on treating the sodium salt of α-benzil monoxime (XLV) with perchloryl fluoride it forms a mixture of benzil monoxime benzoate (XLVI) and benzonitrile:

$$\underset{\text{(XLV)}}{2\,C_6H_5C(=O)C(=N{-}O)C_6H_5} \xrightarrow{FClO_3} \underset{\text{(XLVI)}}{C_6H_5C(=O)C(=N{-}O{-}C(=O)C_6H_5)C_6H_5} + C_6H_5CN.$$

Oximes which do not contain electronegative substituents (acetophenone, benzophenone) are converted into the original ketones under the action of perchloryl fluoride[83].

The possibility of using perchloryl fluoride as an oxidant in analysis has been studied[105]. It was shown that in non-aqueous media at room temperature the aldehyde group is very stable to the action of perchloryl fluoride but the amino- and mercapto-groups undergo complex redox conversions.

Perchlorylation

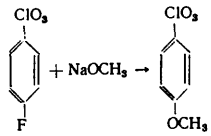
In the presence of a Friedel–Crafts catalyst (usually $AlCl_3$) perchloryl fluoride reacts with aromatic compounds by a type of electrophilic substitution, giving perchlorylaromatic compounds, for example, perchlorylbenzene[106,107]. In the absence of a catalyst the reaction does not take place, but at the same time a complex of the catalyst with perchloryl fluoride was not obtained in the absence of the reagent. Possibly the reaction proceeds through a transition state in which all three components are combined. By analogy with the electrophilic acylation of benzene by Friedel–Crafts, the authors propose the following mechanism for the reaction[107]:

$$FClO_3 + AlCl_3 \rightarrow [FClO_3 \cdot AlCl_3] \rightarrow ClO_3^+ AlFCl_3^-$$
$$C_6H_6 + ClO_3^+ \rightarrow C_6H_5ClO_3 + H^+$$
$$H^+ + AlFCl_3^- \rightarrow HCl\uparrow + AlFCl_2.$$

† The author probably means sodioethyloximinoacetoacetate (Ed. of Translation).

Benzene derivatives (fluorobenzene, phenol, 1,2,3-trifluorobenzene, xylene, etc.) react with perchloryl fluoride. However, the perchlorylation of nitrobenzene and some other aromatic compounds with electronegative substituents could not be carried out.

Perchlorylaromatic compounds are stable in vacuum and steam distillation but can be detonated under severe impact or by a high temperature. They are stable in acid or neutral media but are hydrolysed in strongly alkaline solutions, forming the phenate and chlorate ions. The reaction of halogeno-substituted perchlorylaromatic compounds with alkoxides (and some other reactions with nucleophiles) takes place with retention of the perchloryl group in the nucleus[108], for example:



Reductants such as lithium tetrahydroaluminate, tin(II) chloride in hydrochloric acid, and zinc in hydrochloric acid, do not reduce the ClO_3 group[107], but on a palladium catalyst perchlorylaromatic compounds are readily hydrogenated according to the equation[109]:

$$R{-}C_6H_4{-}ClO_3 + 4\,H_2 \xrightarrow[CH_3COOH]{Pd} RC_6H_5 + HCl + 3\,H_2O.$$

A large number of derivatives are obtained from perchlorylbenzene by the usual methods; they include 4-chloro-, 4-methylthio-, and pentachloro-perchlorylbenzene and 3-perchlorylanilinium chloride. Perchlorylbenzene and its homologues are sulphonated by concentrated sulphuric acid and are nitrated in the *meta*-position by sulphuric–nitric mixture. Azo-, azoxy-, and hydrazo-3-perchlorylbenzenes are also obtained. The infrared spectra of substituted perchlorylbenzenes have been studied[106,107].

Only brief mention has been made of the perchlorylation of alkoxide anions by perchloryl fluoride[56]. With sodium trifluoroethoxide in trifluoroethanol $FClO_3$ gives trifluoroethyl perchlorate and sodium fluoride:

$$F_3CCH_2ONa + FClO_3 \rightarrow F_3CCH_2OClO_3 + NaF.$$

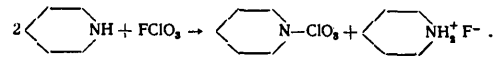
With the less acidic alcohols the reaction does not stop at the stage of the formation of an ester of perchloric acid, but proceeds further by the equation:

$$RO^- \xrightarrow{FClO_3} ROClO_3 \xrightarrow{RONa} ROR + NaClO_4.$$

Thus, sodium ethoxide in ethanol reacts with perchloryl fluoride to give diethyl ether and sodium perchlorate[56].

As already noted, perchloryl fluoride and ammonia give a mixture of ammonium fluoride and the ammonium salt of perchloramide[8,54]. Attempts to carry out an analogous reaction with amines did not lead to the desired result. Perchloryl fluoride reacts with pure amines, usually explosively or forming a complex mixture of oxidation products, usually of the anil type. Aminolysis of perchloryl fluoride by aniline, phenylhydrazine, isopropylamine, isobutylamine, etc. led to the formation of spontaneously explosive solid or liquid substances of unknown structure[110].

Only recently[111] an amine was perchlorylated at the nitrogen. On passing $FClO_3$ into an aqueous solution of piperidine, *N*-perchlorylpiperidine was obtained in 70% yield. This is an unstable liquid, readily hydrolysed by alkalis and highly explosive:



A review has been published[112] part of which is devoted to a consideration of the preparation and properties of perchlorylorganic compounds.

Toxicity

With reference to preliminary tests made on animals, Engelbrecht and Atzwanger[8] characterise perchloryl fluoride as "moderately toxic" 7–8 degrees in Carpenter and coworkers' classification, and give numerical values for LC_{50}: 2000–4000 parts per million in exposure for 4 h. The toxicity of perchloryl fluoride is close to the toxicity of chlorine but without its irritating action[20]. Its odour is detectable in a concentration of 10 parts per million, which is considerably below the permissible concentration on prolonged action. Gall[114] mentions that the toxicity of perchloryl fluoride is low and it does not damage the skin. It was also noted[115] that monkeys can breathe air containing 40 parts per million perchloryl fluoride for a long time but at 200 parts per million slight toxic action is observed.

V. USES

As perchloryl fluoride is a comparatively new substance its possible practical uses are still insufficiently studied. The prospects of using perchloryl fluoride as an oxidant have been considered more than any others. The spectra of flames of some fuel gases with perchloryl fluoride as oxidant have been studied[116] and the rate of flame in mixtures of methane with air on adding perchloryl fluoride has been measured[117]. Schmauch and Servass[115,118] note that the flame of the combination $H_2 + FClO_3$ is readily controlled, has a low background, and can be used with success as a source of excitation in flame photometry.

As an oxidant for rocket propellents[29] liquid perchloryl fluoride in combination with dimethylhydrazine or hydrazine has a specific impulse of 274 s (combustion chamber pressure 42 atm), whereas liquid oxygen with the American fuel JP-4 gives 272 s. In a hybrid, solid–liquid system, perchloryl fluoride gives the same specific impulse as dinitrogen tetroxide, that is, 246 s.[119]

The use of perchloryl fluoride as an oxidant for the high-temperature cutting of metals has been proposed[120].

The possibility of using perchloryl fluoride in other fields is at the discussion stage. There are several patents on its use as a heat transfer medium in refrigeration[121], and as an insecticide–fungicide[122]. The polymerisation of ethylene in the presence of perchloryl fluoride under a pressure of hundreds of atmospheres and a temperature of the order of 200°C has been reported[123].

Thanks to the ability to intensively absorb slow electrons[47] perchloryl fluoride can find application as a gaseous insulator, the dielectric properties of which are better than those of SF_6 and hardly deteriorate on irradiation by γ-rays[21].

Perchloryl fluoride is at present the only agent for obtaining perchlorylaromatic compounds. The latter can find a use for obtaining explosive substances, dyes, and pharmaceutical preparations (3-perchlorylacetanilide, and 4-fluoroperchlorylbenzene exhibit pharmacological potential)[2,106].

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COMPLEX HALIDES IN VAPOURS AT HIGH TEMPERATURES

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I. INTRODUCTION

The extremely rapid development of high temperature chemistry makes necessary the systematic study of the properties of substances in the vapour state. The antiquated ideas about vapour as a medium barren of processes and compounds are now undergoing considerable changes. It is becoming more and more evident that in the variety of forms and peculiarities of their interaction a vapour is often comparable with condensed phases.

Problems of vaporisation and the chemistry and structure of complex molecules in vapour-phase media at high temperatures have repeatedly formed the subject of discussions in monographs and articles. In this connection mention must be made of the works of Margrave [1,2], Searcy [3], Kireev [4], Glemser [5], Novikov [6], Drowart and Goldfinger [7], and some others. They give many examples of polymerisation and complex formation by oxides and halides in vapour form, producing compounds of the hydrate type, salts of oxo-acids, oxide halides, and complex halides. In all the examples considered reference is made only to compounds which exist in the form of neutral molecules, but it may be assumed that in ionised vapour the variety of species will be even greater, since compounds non-existent in the form of neutral molecules can be made stable by addition or loss of electrons and the formation of ionic molecules. Unfortunately, the quantitative physicochemical characteristics of complex vapour-phase molecules — not only ionised but also neutral — are known in very few instances.

The vapour-phase double or complex halides, mainly of the type $MM'X_n$, where M is an alkali metal, M' a metal of another group, and X a halogen are better studied in this respect than other compounds. The review given below will be restricted to these forms alone and will not be concerned with compounds of the type $BeAlCl_5$,[8] In_xCl_y,[9] $SiBCl_5$,[10] etc., which have been studied less extensively.

The practical importance of investigations in the region defined above is obvious, since under industrial conditions many metals are obtained either by electrolysis of molten salt mixtures (including salts of the alkali metals), or by metallothermic reduction of halides.

The study of complexes in vapour form is of great theoretical interest above all for the further development of the chemistry of coordination compounds.

II. COMPLEX HALIDES IN VAPOUR FORM

The simplest representatives of complex compounds of the type $MM'X_n$ in the vapour state are the mixed dimers of alkali metal halides.

As already mentioned, the alkali metal halides exist in vapours in the form of a collection of monomeric, dimeric, and some more complex molecules. However, the relation between the monomer and various polymeric forms is such that for most purposes only dimerisation need be considered and the more complex forms are essential only for lithium halides [11-13].

The stability of the vapour forms of the dimers of the alkali metal halides falls from Li to Cs, as is shown by the data [14] given in Table 1.

In the interaction of dimeric molecules of the various alkali metal halides the constituent parts can be interchanged as a result of which mixed dimers are obtained. Thus data have been given for the reaction [15]:

(1) $(Li_2F_2) + (Na_2F_2) = 2(NaLiF_2)$ $\Delta H^\circ_{1000} = 0.$

The results of a mass spectrometric investigation [16] of equilibria in the disproportionation by stepwise replacement are known:

(2) $(CsRbF_2) = {}^1/_2(Rb_2F_2) + {}^1/_2(Cs_2F_2)$ ΔH°_{904} 1.3 kcal mole^{-1},
(3) $(RbKF_2) = {}^1/_2(K_2F_2) + {}^1/_2(Rb_2F_2)$ ΔH°_{980} 1.4 kcal mole^{-1},
(4) $(KNaF_2) = {}^1/_2(Na_2F_2) + {}^1/_2(K_2F_2)$ ΔH°_{925} 1.5 kcal mole^{-1},
(5) $(NaLiF_2) = {}^1/_2(Li_2F_2) + {}^1/_2(Na_2F_2)$ ΔH°_{1173} 2.3 kcal mole^{-1},
(6) $(RbLiF_2) = {}^1/_2(Li_2F_2) + {}^1/_2(Rb_2F_2)$ ΔH°_{985} 3.0 kcal mole^{-1}.

In the mass spectrometric analysis of the composition of the vapour over LiCl–MCl mixtures [17] (M = Na, K, Rb, Cs) the ions $LiCl^+$, Li_2Cl^+, M^+, MCl^+, M_2Cl^+, and $LiMCl^+$ were observed in the molecular beam. The ion $LiMCl^+$ could be a fragment of molecules of mixed dimers. Analogous results were obtained by Novikov and coworkers [18], but in addition the ion Cs_2LiCl^+ was observed, which the authors took to be a fragment of a molecule of the mixed trimer Cs_2LiCl_3. Thermodynamic characteristics have also been given [18-21] for the disproportionation of the following mixed dimers:

		ΔH°_T, kcal mole^{-1}	t, °C
(7)	$(RbNaCl_2) = {}^1/_2(Rb_2Cl_2) + {}^1/_2(Na_2Cl_2)$	5.8	800
(8)	$(RbKCl_2) = {}^1/_2(Rb_2Cl_2) + {}^1/_2(K_2Cl_2)$	0	800
(9)	$(CsLiCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(Li_2Cl_2)$	7.0	650—900
(10)	$(CsNaCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(Na_2Cl_2)$	5.2	650—900
(11)	$(CsKCl_2) = {}^1/_2(Cs_2Cl_2) + {}^1/_2(K_2Cl_2)$	2.7	650—900

TABLE 1. Thermodynamic characteristics of the process $(M_2X_2) = 2(MX)$.

		Li	Na	K	Rb	Cs
Fluorides	ΔH°_{1000}, kcal mole^{-1}	61.5	56.9	49.6	43.9	39.2
	ΔS°_{1000}, e.u.	34.0	31.6	32.4	29.4	30 5
Chlorides	ΔH°_{1000}, kcal mole^{-1}	52.1	48.5	44.5	41.7	39.0
	ΔS°_{1000}, e.u.	32.1	29.0	28.4	28.1	28.0

It should be noted that the substitutions (2)–(11) are exothermic and the thermal effect is the greater the further apart the alkali metals, that is, the greater the difference in properties of their compounds. With increase in this difference the molecule of the mixed dimer becomes less and less symmetrical; the halogen atoms become more and more displaced towards one of the alkali metal atoms, which thus acquires the function of complex formation. To compare the mixed and true dimers as regards stability in the vapour state we will examine the thermodynamic scheme:

Scheme 1

$(M_2X_2) = 2(MX)$	ΔH_1°	$\Delta S_1^\circ \simeq 30$ e.u.
$(M'_2X_2) = 2(M'X)$	ΔH_2°	$\Delta S_2^\circ \simeq 30$ e.u.
$(MM'X_2) = {}^1/_2(M_2X_2) + {}^1/_2(M'_2X_2)$	ΔH_3°	$\Delta S_3^\circ \simeq 0$
$(MM'X_2) = (MX) + (M'X)$	ΔH_4°	ΔS_4°

It is easy to see that:

$$\Delta H_4^\circ = {}^1/_2(\Delta H_1^\circ + \Delta H_2^\circ) + \Delta H_3^\circ$$
$$\Delta S_4^\circ = {}^1/_2(\Delta S_1^\circ + \Delta S_2^\circ) \quad 30 \text{ e.u.} \qquad (B)$$

Hence the change in entropy during the dissociation of simple and mixed dimers is approximately the same, but the enthalpy of dissociation of the mixed dimer (ΔH_4) is greater than the arithmetic mean of the enthalpies of dissociation of the simple dimers by the quantity ΔH_3. Consequently in stability the mixed dimer will approximate to the more stable of the simple dimers, that is, the dimer which has the strongest M–Cl bond.

Since the stability of the dimers falls from Li to Cs (that is, with increase in the ionic radius), in the mixed dimer the ion with the smaller radius will function as the complex-forming atom.

We shall now consider the vapour-phase double compounds formed by the alkali metal chlorides with the dichlorides of some other metals.

The formation of a vapour-phase complex species was first proposed by the investigators of the BeF_2–NaF binary system[22], since this was the most rational explanation for unusual observations on the pressure and composition of the vapour. From the location of the maximum on the curve for the partial pressure of NaF calculated by the Duhem–Margules equation (without allowance for the pressure of the double species) the composition of the complex was found to be $NaBeF_3$. Berkowitz and Chypka[23] observed the analogous compound of beryllium and lithium fluorides (more correctly the ion $LiBeF_2^+$) in a mass spectrometric investigation of the composition of the vapour in the BeF_2–LiF system. For the process:

(12) $(LiBeF_3) = (LiF) + (BeF_2)$

they obtained the value $\Delta H^\circ_{900} = 53$ kcal mole^{-1}.

Many papers only qualitatively justify the assumption of a double compound in the vapour, although the experimental results sometimes allow the composition of the vapour to be calculated.

Among such studies is an investigation of the $BeCl_2$–NaCl and $BeCl_2$–KCl systems[24], the study of the BeF_2–NaF system[22] mentioned above, the work of Barton and Bloom[25] (who studied the formation of double compounds by lead and cadmium chlorides), an article with data on the KCl–$MgCl_2$ system[26], and work on the pressure and composition of the vapour in the $CaCl_2$–KCl and KCl–$SrCl_2$ systems[27]. The formation of $KCoCl_3$, $KNiCl_3$, K_2CdCl_4, and $KZnCl_3$ in the vapour has been proposed[28,29].

Novikov and Kuz'menko[30,31], using published data[22,24,26,27], calculated the thermodynamic characteristics of the dissociation processes of some double chlorides, namely:

	T, °C	ΔH°_T, kcal mole^{-1}	ΔS°_T, e.u.
(13) $(NaBeF_3) = (NaF) + (BeF_2)$	900	52±2	21±3
(14) $(NaBeCl_3) = (NaCl) + (BeCl_2)$	720	54±5	23±2
(15) $(KBeCl_3) = (KCl) + (BeCl_2)$	720	48±5	24±2
(16) $(KMgCl_3) = (KCl) + (MgCl_2)$	1080	58±5	31±2
(17) $(KCaCl_3) = (KCl) + (CaCl_2)$	1100	63±3	30±2
(18) $(KSrCl_3) = (KCl) + (SrCl_2)$	1100	67±17	32±13

The decrease in stability of the double compound $KM'Cl_3$ in the sequence Sr–Be was attributed by the authors[31] to the mutual repulsion of the ligands, the force of which rises in the order Sr–Be.

The change in the stability of the double chlorides along the alkali metal series can be seen in the example of the compounds $MFeCl_3$, the thermodynamic characteristics of the dissociation of which have been given[23,28]:

		ΔH°_T, kcal mole^{-1};
(19)	$(LiFeCl_3) = (LiCl) + (FeCl_2)$	43.0
(20)	$(KFeCl_3) = (KCl) + (FeCl_2)$	34.7
(21)	$(CsFeCl_3) = (CsCl) + (FeCl_2)$	24.7

Obviously, the stability of the double compounds falls from Li to Cs, that is, in the same sequence as the stability of the dimeric alkali metal chlorides.

We shall now consider the thermodynamic characteristics of the vapour-phase complexes in the MCl–$M'Cl_3$ and MF–$M'F_3$ systems.

As in the above examples, the formation of vapour-phase double compounds by the elements of Periodic Groups I and II, the information concerning the compounds of type $MM'X_4$ relate mainly to the fluorides and chlorides.

A large number of investigations have disclosed the formation of volatile double compounds in MCl–$AlCl_3$ and MF–AlF_3 systems.

The existence of the compound $NaAlF_4$ has been shown by X-ray analysis[32] of the condensate obtained on vaporisation of a melt with equimolecular amounts of NaF and AlF_3. An investigation of the condensate obtained by passing an inert gas over AlF_3–NaF melt led Howard[33] to conclude that the volatile compound $NaAlF_4$ existed.

The existence of $NaAlF_4$ in the vapour was confirmed by investigations of the pressure and composition of the vapour in the AlF_3–NaF system made by Vetyukov and coworkers[34] and also Ginsberg and Böhme[35].

Porter and Zeller[36], in studying the AlF_3–LiF system mass spectrometrically, observed two double compounds in the vapour: $LiAlF_4$ and $Li_2Al_2F_8$ (or Li_2AlF_5). These authors calculated the thermodynamic characteristics of the equilibrium:

(22) $(LiAlF_4) = (LiF) + (AlF_3)$ $\Delta H^\circ_{1000} = 73$ kcal mole^{-1}; $\Delta S^\circ_{1000} = 37$ e.u.

As regards the analogous systems of aluminium and alkali metal chlorides, mention must be made of the studies of Naryshkin[37], Plotnikov and coworkers[38], Morozov and coworkers[39,40], and Grothe[41].

An approximate value of the ΔH°_{T} for the equilibrium

(23) $(NaAlCl_4) = (NaCl) + (AlCl_3)$

is ~ 50 kcal mole^{-1}, given by Dewing[42]; this equilibrium was studied in detail by Galitskii[43] with the aid of a combination of tensimetry and analysis of the condensates. He obtained the thermodynamic characteristics:

$$\Delta H^{\circ}_{970} = 49.2 \pm 2 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{970} = 28.9 \pm 2 \text{ e.u.}$$

In the same work[43] data are given for the equilibria:

(24) $(NaFeCl_4) = (NaCl) + (FeCl_3)$ $\Delta H^{\circ}_{970} = 51.6 \pm 2,5$ kcal mole^{-1}; $\Delta S^{\circ}_{970} = 28.9$ e.u.

(25) $(Na_3CrCl_6) = 3(NaCl) + (CrCl_3)$ $\Delta H^{\circ}_{1180} = 139.0 \pm 10$ kcal mole^{-1}; $\Delta S^{\circ}_{1180} = 74.0 \pm 7$ e.u.

(26) $(K_3CrCl_6) = 3(KCl) + (CrCl_3)$ $\Delta H^{\circ}_{1180} = 132.0 \pm 10$ kcal mole^{-1}; $\Delta S^{\circ}_{1180} = 76.0 \pm 7$ e.u.

These results are quite interesting although in the last two examples the correctness of the formula selected for the double compound seems doubtful.

Richards and Gregory[44] investigated the $FeCl_3$–NaCl system by a flow method, passing the vapour of $FeCl_3$ over solid NaCl. For the equilibrium:

(27) $[NaCl] + (FeCl_3) = (NaFeCl_4)$

they obtained the following thermodynamic characteristics:

$$\Delta H^{\circ}_{723} = 3.7 \pm 1 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{723} = 6.5 \pm 1.5 \text{ e.u.}$$

When the equilibrium is recalculated for NaCl vapour, we obtain:

$$\Delta H^{\circ}_{723} = 51.3 \pm 1 \text{ kcal mole}^{-1}; \Delta S^{\circ}_{723} = 29.5 \pm 1.5 \text{ e.u.},$$

that is, values very close to those obtained by Galitskii[43].

Cook and Dann[45], after analysing vapour pressure data for MCl–$FeCl_3$ systems, concluded that vaporisation of the compounds $NaFeCl_4$ and $KFeCl_4$ was possible.

As can be concluded from the above examples, the vapour-phase double compounds of aluminium and iron have the formula $MM'X_4$ in the great majority of instances.

French investigators, in studying the AlF_3–NaF system by the flow and boiling point methods[46], suggested the existence of a heavy vapour-phase molecule, $Na_5Al_3F_{14}$, but this is very improbable. In preferring the form $MM'X_4$ for the vapour phase double compounds of alkali metal chlorides with the trichlorides of other elements we are convinced by the tensimetric and mass-spectrometric investigations of the MCl–$LnCl_3$ systems, where Ln is a rare-earth element (r.e.e.). In the mass-spectrometric analysis of the composition of the vapour over mixtures of the chlorides KCl–$ErCl_3$,[47] NaCl–$LnCl_3$ (Ln = Nd, Er, Y)[48], LiCl–$NdCl_3$,[48] and CsCl–$NdCl_3$ and CsCl–$ErCl_3$,[49] in addition to the ions corresponding to the simple chlorides, the ion $MLnCl_3^+$ has been recorded; this is a fragment of the double chloride molecule $MLnCl_4$.

The thermodynamic characteristics of the dissociation of the complex:

(28) $(MLnCl_4) = (MCl) + (LnCl_3)$

were calculated, starting from the values of

$$K_{equil} = \frac{P_{MCl} P_{LnCl_3}}{P_{MLnCl_4}}$$

for various temperatures. The necessary partial pressures of the components of the vapour were found strictly by the method proposed by Novikov and Gavryuchenkov[50] for the systems $ErCl_3$–KCl,[50] $LaCl_3$–NaCl,[51] NaCl–$NdCl_3$,[48] CsCl–$NdCl_3$ and CsCl–$ErCl_3$,[49] and with some assumptions for the $ErCl_3$–NaCl [52] and KCl–$LnCl_3$ systems[53] (Ln = La, Ce, Pr, and Nd). To calculate the composition of the vapour in these systems we used data on the saturated vapour pressure obtained by tbe boiling point method[54], and information on the gross composition of the vapour obtained by analysis of the condensates.

Table 2 gives the values of the thermodynamic characteristics of the dissociation of $MLnCl_4$, taken from the works cited above[48-53]. It suggests that the stabilities of the r.e.e. chloro-complexes are similar. Along the alkali metal series Na–K–Cs their stability changes in the same sequence as for the dimers of the alkali metal halides. As shown above, there is the same change in stability for the double halides of type $MM'X_3$.

The data are still insufficient to decide reliably how the stability of the $MM'X_4$ double chlorides changes with the nature of the complex-forming element, but since $NaLaCl_4$ is more stable than the corresponding aluminium double chloride by almost 20 kcal mole^{-1} and the double chlorides of boron decompose at ~ 300° without passing into the vapour[55], it can be taken that in the sequence B–Al–La the stability of the double chlorides will increase.

Let us now consider the formation of vapour-phase double compounds of the elements of Periodic Group IV.

The halides of elements in the quadrivalent state have less tendency to form stable double compounds in vapour form than those of elements in a bivalent or tervalent state.

Thus Flengas and Ingraham[56], who studied the behaviour of K_2TiCl_6 in heating, found that this compound, without passing into the vapour, decomposes according to the scheme:

(29) $[K_2TiCl_6] = 2[KCl] + (TiCl_4)$ $\Delta H^{\circ} = 26.4$ kcal mole^{-1}; $\Delta S^{\circ} = 33.3$ e.u.

Just as in the systems CsCl–$TiCl_4$ and RbCl–$TiCl_4$,[57] NaCl–$ZrCl_4$,[58-60] KCl–$ZrCl_4$,[59] and CsCl–$ZrCl_4$,[61] so also in the analogous systems with $HfCl_4$ [61,62] the double compounds do not pass into the vapour, but decompose to form $ZrCl_4$ or $HfCl_4$ vapour.

$ThCl_4$, which is even less volatile, can form a rather stable vapour-phase double chloride[63] with potassium chloride:

(30) $(KThCl_5) = (KCl) + (ThCl_4)$ $\Delta H^{\circ}_{1280} = 49.3 \pm 3$ kcal mole^{-1}; $\Delta S^{\circ}_{1280} = 28.0 \pm 3$ e.u.

TABLE 2. Values of ΔH°_{T}, kcal mole^{-1}, and ΔS°_{T}, e.u., for the dissociation of compounds in the vapour phase.

Compound		Ln				
		La	Ce	Pr	Nd	Er
$NaLnCl_4$	ΔH°_{1400}	69.8	—	—	61.3	63.0
	ΔS°_{1400}	32.8	—	—	32 6	34.0
$KLnCl_4$	ΔH°_{1350}	61.4	61.0	59.3	59.3	59.5
	ΔS°_{1350}	32.6	32.6	32.6	32.6	32.6
$CsLnCl_4$	ΔH°_{1300}	—	—	—	57.2	58.0
	ΔS°_{1300}	—	—	—	29.8	30.8

The authors[63] based the calculation for this system on the pressure and gross composition of the vapour. The form of the compound is determined by analogy with the form of the double fluoride in the $NaF-ZrF_4$ system. The latter system was investigated in detail by Sidorov[64,65]. As a result of the mass spectrometric study of the composition of the vapour in the $NaF-ZrF_4$ system he found that the compound corresponds to the formula $NaZrF_5$ and the value of ΔH_T° was calculated for the process:

(31) $(NaZrF_5) = (NaF) + (ZrF_4)$ $\Delta H^\circ_{1170} = 64.4$ kcal mole^{-1}.

Sense and coworkers[66,67] give for this process very similar values for the thermodynamic characteristics:

$$\Delta H^\circ_{1300} = 67 \text{ kcal mole}^{-1};\ \Delta S^\circ_{1170} = 29 \text{ e.u.}$$

and also suggest the formation of volatile fluorides in the ZrF_4-MF systems (M = Li, Rb).

Comparison of the data for the $NaCl-ZrCl_4$ [58-60] and $NaF-ZrF_4$ [64-67] systems indicates that double compounds of fluorides are more stable than the analogous compounds of chlorides, and this conclusion can evidently be taken as general.

Reverting to the complex chlorides, it is interesting to compare the stability of the double compounds of Groups I, II, III, and IV. Table 3 gives the values of the thermodynamic characteristics of the dissociation of some vapour-phase double compounds.

The choice of the elements in Table 3 is not fortuitous. From their position in the Periodic Table, K, Sr, La, and Th are diagonal analogues, which permits a comparison of the thermodynamic properties of monotypical compounds of these elements.

On comparing the quantities in Table 3, it is seen that there are extrema in the stability characteristics of the vapour-phase double chlorides of the type $KMCl_n$ as n goes from 2 to 5.

Extrema occur because the stability of the vapour-phase double compounds is influenced by at least two opposing tendencies: on the one hand, increase in the charge of the nucleus of the atom of the complex-forming element in the series K–Sr–La–Th, on the other, an increase in the coordination number, and consequently a rise in the repulsion energy of the ligands (Cl) for one another.

The increase in stability of the compounds $MM'Cl_n$ on going down the groups of the Periodic Table which we noted earlier becomes understandable from this point of view, since the coordination number here remains unchanged, whereas the size of the atom of the complex-forming element increases, and consequently the energy of repulsion of the ligands falls.

It is also interesting to note that double compounds which are stable in the vapour are formed when the chlorides reacting have similar volatility. On the other hand, if one of the chlorides has much greater volatility than the other, then the degree of association and the energy of complex formation in the vapour are much less. This can be illustrated by the examples quoted above for reactions in the systems $KCl-M'Cl_4$ (M' = Ti, Zr, Hf, Th). At the same temperature the saturation vapour pressures of titanium, zirconium, and hafnium chlorides are respectively 10^{12}, 10^7, and 10^8 times the vapour pressure of KCl. As already noted, these chlorides do not form volatile double compounds. On the other hand, $ThCl_4$, which has a saturation vapour pressure almost the same as that of KCl, forms the stable vapour-phase compound $KThCl_5$.

TABLE 3.

Equilibrium	ΔH°_T, kcal mole^{-1}	ΔS°_T, e.u.	Reference
$(KKCl_2) = (KCl) + (KCl)$	44.5	28.4	9
$(KSrCl_3) = (KCl) + (SrCl_2)$	67	32	25
$(KLaCl_4) = (KCl) + (LaCl_3)$	61	33	47
$(KThCl_5) = (KCl) + (ThCl_4)$	49	28	56

In conclusion we shall refer to the problem of the vaporisation of ammonium double halides. The facts given above show that double chlorides of the type $MM'Cl_n$ are rather involatile compounds, but stable in the vapour. On the other hand, double chlorides based on ammonium chloride are thought by many authors to be readily volatile.

Thus, Morozov and Toptygin[68], in studying the $AlCl_3-NH_4Cl$ system by the flow method, supposed that the compound NH_4AlCl_4 volatilises without decomposition and found its boiling point to be 402°. In the same system results obtained[69] by a static method indicate that the composition with 50 mole % has maximal boiling point.

Investigators of the $NH_4Cl-FeCl_3$ system[70] found that the compound $FeCl_3.NH_4Cl$ not only exhibits a congruent melting point, but also boils without decomposition and the boiling point of the melt with 50 mole % composition is maximal, as in the $NH_4Cl-AlCl_3$ system.

Li[71] states that $(NH_4)_2SnCl_6$ sublimes at 412°, whereas the alkali metal hexachlorostannates decompose without entering the vapour.

Note that in all the studies mentioned above there is no direct proof of the existence of double chlorides of the type $NH_4M'Cl_x$ in vapour form.

The conclusion that the ammonium double chlorides vaporise (or sublime) without decomposition is usually based on the fact that the condensate obtained in the vaporisation has the same composition as the initial compound. However, when the double compound is formed by ammonium chloride and a rather volatile chloride ($AlCl_3$, $FeCl_3$, $SnCl_4$, etc.) the composition of the condensate and the original compound will be the same even if the compound dissociates completely in the vapour but then is formed again on condensation, as happens in the vaporisation of NH_4Cl. When the double compound is formed by ammonium chloride and another relatively more involatile chloride, then such behaviour is impossible and the composition of the condensate will not correspond to the composition of the compound, as for example, in the $NH_4Cl-ZnCl_2$ and $NH_4Cl-CdCl_2$ systems[70]. Such behaviour by ammonium salts is easy to explain qualitatively. It is well known that the stabilisation of such forms is connected with the formation of the NH_4^+ ion. On transfer to the vapour the degree of ionicity of the bonds in the molecules drops sharply, which in ammonium compounds should lead to marked weakening of them.

Hence there is still no single opinion concerning the formation of ammonium double chlorides in vapour form.

III. INCREASE IN THE THERMAL STABILITY OF COMPLEX HALIDES ON VAPORISATION

To determine whether strengthening or weakening of bonds in complex chlorides occurs on vaporisation it is obviously necessary to compare their stability in relation

to dissociation into simple chlorides in the condensed and vapour states.

The dissociation of double chlorides in these states of aggregation can be related to one another by the following scheme:

Scheme 2

$[MM'Cl_{n+1}] = [MCl] + [M'Cl_n]$	ΔH_1°;	ΔS_1°
$[MCl] = (MCl)$	ΔH_2°;	ΔS_2°
$[M'Cl_{n+1}] = (M'Cl_n)$	ΔH_3°;	ΔS_3°
$[MM'Cl_{n+1}] = (MM'Cl_n)$	ΔH_4°;	ΔS_4°
$(MM'Cl_{n+1}) = (MCl) + (M'Cl_n)$	ΔH_5°;	ΔS_5°

$$\Delta H_5^\circ - \Delta H_1^\circ = (\Delta H_2^\circ + \Delta H_3^\circ) - \Delta H_4^\circ,$$
$$\Delta S_5^\circ - \Delta S_1^\circ = (\Delta S_2^\circ + \Delta S_3^\circ) - \Delta S_4^\circ.$$

According to Scheme 2, bond strengthening in the compound on passing into the vapour is determined by the difference in the thermodynamic characteristics of the first and last processes and appears as the result of the competition of the volatility of the double chloride (ΔH_4°) and of the dissociation products (ΔH_2° and ΔH_3°).

The quantities ΔS_2°, ΔS_3°, and ΔS_4° vary little for the different halides; therefore the difference ($\Delta S_2^\circ + \Delta S_3^\circ$) - ΔS_4° can be taken as constant at ~ 25 e.u. At 1000–1300°K such a change in entropy will correspond with a change in free energy of 25–30 kcal mole^{-1}, that is,

$$\Delta G_5^\circ - \Delta G_1^\circ = (\Delta H_5^\circ - \Delta H_1^\circ) - (25-30)T.$$

Consequently, the strengthening of the double compounds will take place if (ΔH_5° - ΔH_1°) ≥ 25–30 kcal mole^{-1}. From the relation

$$\Delta H_5^\circ - \Delta H_1^\circ = (\Delta H_2^\circ + \Delta H_3^\circ) - \Delta H_4^\circ$$

it can be concluded that the quantities ΔH_2, ΔH_3, and ΔH_4 (that is, the volatility characteristics of the simple and double chlorides) determinine the strengthening or weakening of binding in the double compound on passage into the vapour and, consequently, also the possibility of its existence. Let us examine this question by specific examples.

In the first example we will examine the vapour-phase double chlorides of the r.e.e. and potassium.

For the dissociation of these compounds:

(32) $$(KLnCl_4) = (KCl) + (LnCl_3),$$

where Ln = La, Ce, Pr, Nd, and Er, very similar thermodynamic characteristics have been proposed[50-53].

$$\Delta H_{1350}^\circ = 60 \text{ kcal mole}^{-1};\quad \Delta S_{1350}^\circ = 32.6 \text{ e.u.}$$

In the same studies the following characteristics have been proposed for the sublimation of the double chloride:

(33) $$[KLnCl_4] = (KLnCl_4)\ \Delta H_T^\circ = (60—70) \text{ kcal mole}^{-1};\ \Delta S_T^\circ = 41 \text{ e.u.}$$

Hence in the example under consideration both the double chlorides and their dissociation products are of low volatility. Thus, for $LnCl_3$ (ΔH_S° = 75–65 kcal mole^{-1}, ΔS_S° = = 45–42 e.u.)[72] and for KCl (ΔH_S° = 53.3 kcal mole^{-1}, ΔS_S° = = 33.3 e.u.)[14], the value of ΔH_4° according to Baev's estimate[73] is ~ 4–6 kcal; therefore the difference (ΔH_2° + ΔH_3°) - ΔH_4° will here be greater than the quantity ~ 55 kcal mole^{-1}, which ensures strengthening of the bonds in the complex during vaporisation.

We will consider a second, frequently encountered, example that occurs when the double compound and one of the dissociation products is of low volatility but the other is volatile.

The two chlorides of different volatility KCl and $TiCl_4$ (ΔH_e = 9.6 kcal mole^{-1}) form a compound K_2TiCl_6, which, as is well known[56], decomposes above 300°:

(34) $$[K_2TiCl_6] = 2[KCl] + (TiCl_4) \qquad \Delta H_{920}^\circ = 26{,}4 \pm 1.3 \text{ kcal mole}^{-1};\quad \Delta S_{920}^\circ = 28{,}5 \pm 2.3 \text{ e.u.}$$

This process proceeds without noticeable appearance of potassium chloride in the condensate† which could serve as an indication of the formation of the double compound in the vapour to even a slight extent. We will compare this reaction with the hypothetical appearance in the vapour of $KTiCl_5$ (by analogy with $NaZrF_5$):[55]

(35) $$[K_2TiCl_6] = [KCl] + (KTiCl_5).$$

Let the experimentally imperceptible equilibrium in the vapour:

$$(KTiCl_5) = (KCl) + (TiCl_4),$$

be characterised by the value ΔS° = 28 e.u., like the analogous process of the dissociation of $KThCl_5$:[63]

$$\Delta H_{610}^\circ = 27 \text{ kcal mole}^{-1}.$$

Let us draw up Scheme 3:

Scheme 3

		ΔH kcal mole^{-1}	ΔS, e.u.
(a)	$[K_2TiCl_6] = 2[KCl] + (TiCl_4)$	ΔH_1°=26.4	ΔS_1°=33.3
(b)	$[KCl] = (KCl)$	ΔH_2°=50.2	ΔS_2°=32,6
(c)	$(KTiCl_5) = (KCl) + (TiCl_4)$	ΔH_3°= (≤32)	ΔS_3°= (28)
(d)	$[K_2TiCl_6] = [KCl] + (KTiCl_5)$	ΔH_4° (≥45)	ΔS_4°= (38)

From the experimental data on the vapour pressure of ($TiCl_4$) over $[K_2TiCl_6]$ 1 atm is reached at 798°K. Let us suppose that the condition of near involatility of the double compound at this temperature corresponds to a $KTiCl_5$ pressure ≤ 10^{-4} atm. Starting from this value at ΔS_4° = = 38 e.u. we find for equilibrium (*d*) $\Delta H_4^\circ \geq 45$ kcal mole^{-1}, whence for equilibrium (*c*) we obtain $\Delta H_3^\circ \leq 32$ kcal mole^{-1}. If on the basis of these quantities we calculate ΔG_T° of stabilisation according to Scheme 2, we obtain ΔG_T° = = 28 - $T \times 28 \times 10^{-3}$ kcal mole^{-1} from whence it follows that in the vapour $KTiCl_5$ has enhanced stability only up to 1000°K, when its volatility is negligible, whereas under these conditions the decomposition of $[K_2TiCl_6]$ with formation of ($TiCl_4$) has already ceased.

† In the analogous NaCl–$ZrCl_4$ system Korschunov and Gregory[60] note a little NaCl in the condensate but explain this by entrainment of dust. According to their results the only process is:

(36) $$[Na_2ZrCl_6] = 2[NaCl] + (ZrCl_4)\quad \Delta S_{610}^\circ = 28 \text{ e.u.}$$

The following example, in which a rather difficultly volatile compound decomposes on heating to give two readily volatile compounds, is encountered comparatively rarely. An example is the equilibrium:

$$(37)\qquad [NH_4Cl] = (NH_3) + (HCl) \qquad \begin{matrix}\Delta H^\circ_{298} = 42.4 \text{ kcal mole}^{-1},\\ \Delta S^\circ_{298} = 68.4 \text{ e.u.}\end{matrix}$$

The values ΔH° = 9.4 kcal mole^{-1} and ΔS° = 3.1 e.u. have been proposed[74-76] for the dissociation of ammonium chloride in the vapour:

$$(38)\qquad (NH_4Cl) = (NH_3) + (HCl).$$

Combining these two equilibria, for the sublimation of ammonium chloride we obtain ΔG° = 33 000 - 37T, from which at T = 620°K the saturated vapour pressure of $NH_4Cl \simeq 0.3$ mm, whereas at this temperature its dissociation pressure reaches 1 atm.

These examples lead to the following conclusions.

1. A double compound can be present in vapour in appreciable quantities if the thermodynamic characteristics of its volatility are close to the analogous quantities for the dissociation products.

2. The lower the volatility of the dissociation products (that is, the greater ΔG°_2 and ΔG°_3 in Scheme 2), the more stable the initial compound in the vapour state (the greater ΔG°_5) and the more it is stabilised on transfer to the vapour (the greater the difference ΔG°_5 - ΔG°_1).

On the other hand, if we write the balance equation compiled according to Scheme 2 in the following form:

$$\Delta G^\circ_5 + \Delta G^\circ_4 = \Delta G^\circ_1 + \Delta G^\circ_2 + \Delta G^\circ_3,$$

then we see that in each specific instance the sum ΔG°_5 + + ΔG°_4, that is, the sum of the characteristics of stability and volatility of the double compound, will be constant. This signifies that the greater the volatility of the double compound (the less ΔG°_4), the greater its stability in the vapour state (the greater ΔG°_5).

IV. CONNECTION BETWEEN COMPLEX FORMATION AND DIMERISATION OF COMPOUNDS IN THE VAPOUR STATE

In considering the vapour states of complex compounds formed by the halides of the alkali metals with those of the elements of Periodic Groups II, III, and IV, it is noted[7,48-52] that their stability alters along the series of alkali metals symbathically with the stability of the dimeric alkali metal chlorides. The same symbathic nature is observed in the change in stability of the complex chlorides and dimeric molecules of chlorides of complex-forming elements.

For example, the heats of dissociation of the $KMgCl_3$ and $KBeCl_3$ molecules[30] are 58.0 and 48.0 kcal mole^{-1}, but those of the dimers[77,78] Mg_2Cl_4 and Be_2Cl_4 are 39.2 and 23.0 kcal mole^{-1} respectively. Hence the molecule of the complex chloride as it were inherits the properties of the dimeric molecules of the initial chlorides. The vapour-phase complex chlorides, like the vapour-phase dimers of the simple chlorides, are usually formed by two molecules, for example, $KMgCl_3$, $NaAlCl_4$, $MLnCl_4$, $KThCl_5$, etc., that is, in form these are substituted dimers, formed not by the same, but by different molecules.

Complex chlorides composed of more than two molecules of simple chlorides are encountered very rarely; just as in the vaporisation of pure chlorides the vapour consists mainly of monomeric and dimeric molecules, but trimers and higher molecular weight polymers are usually observed in much smaller proportions.

The formation of molecules of complex chlorides can be represented as a substitution:

$$(39)\qquad (M_2Cl_{2n}) + (M'_2Cl_{2m}) = 2(MM'Cl_{n+m}).$$

When the reacting dimers have similar properties the heat of substitution is close to zero, for example[16,20]:

$$(40)\qquad (Rb_2Cl_2) + (K_2Cl_2) = 2(RbKCl_2)\quad \Delta H^\circ \simeq 0$$
$$(41)\qquad (Na_2F_2) + (K_2F_2) = 2(NaKF_2)\quad \Delta H^\circ = -2.9 \text{ kcal mole}^{-1}.$$

On going to the double compounds of the alkali metal chlorides with the chlorides of the elements of Periodic Groups II and III the difference in properties of the simple chlorides rises, and there is a corresponding increase in the ΔH° of the substitution. For example[30,43]:

$$(42)\qquad (Na_2Cl_2) + (Al_2Cl_6) = 2(NaAlCl_4)\quad \Delta H^\circ = -27 \text{ kcal mole}^{-1}$$
$$(43)\qquad (Na_2Cl_2) + (Be_2Cl_4) = 2(NaBeCl_3)\quad \Delta H^\circ = -22 \text{ kcal mole}^{-1}.$$

According to Scheme 1 considered above, in its stability to dissociation into simple chlorides a double chloride either approaches the more stable dimer or surpasses it, depending on the heat of substitution. In this connection the concentration of the double chloride in the vapour is either greater than that of each of the dimers or approximately the same as the more stable of the dimers. To illustrate this position we will consider Scheme 4:

Scheme 4

$[MCl_n] = (M_2Cl_{2n})$	ΔH_1	ΔS_1
$[M'Cl_m] = (M'_2Cl_{2m})$	ΔH_2	ΔS_2
$MM'Cl_{n+m}] = [MCl_n] + [MCl_m]$	ΔH_3	ΔS_3
$MM'Cl_{n+m}) = {}^1/_2(M_2Cl_{2n}) + {}^1/_2(M'_2Cl_{2m})$	ΔH_4	$\Delta S_4 \simeq 0$
$[MM'Cl_{n+m}] = (MM'Cl_{n+m})$	ΔH_5	ΔS_5

$\Delta H_5 = {}^1/_2(\Delta H_1 + \Delta H_2) + (\Delta H_3 - \Delta H_4)$
$\Delta S_5 = {}^1/_2(\Delta S_1 + \Delta S_2) + \Delta S_3$

Usually $\Delta H_4 > \Delta H_3$; therefore the enthalpy of sublimation of the complex chloride (ΔH_5) is less than the arithmetic mean of the heats of sublimation of the dimers ($\frac{1}{2}\Delta H_1 + \frac{1}{2}\Delta H_2$). At the same time the change in the entropy of sublimation of the complex chloride is greater than the arithmetic mean of the entropies of sublimation of the dimers by the quantity ΔS_3, since $\Delta S_4 \simeq 0$ as the entropy of a reaction proceeding without change in the number of moles of gas.

In this connection the sublimation of a complex chloride can be energetically more favourable than the sublimation of dimers and therefore its concentration in the vapour is significant even when the dimerisation of one of the chlorides is experimentally imperceptible.

From this point of view the existence in the vapour of a complex chloride can indicate the possibility of dimerisation of the simple chlorides which form it.

When the thermodynamic characteristics of the dissociation of a complex chloride (ΔH°_1 and ΔS°_1) are known, for

example, for $KM'Cl_{n+1}$, then the energy‡ of dimerisation of a chloride MCl_n can be calculated by the method already proposed[6]. The thermodynamic Scheme 5 is drawn up:

Scheme 5

$(KM'Cl_{n+1}) = (KCl) + (M'Cl_n)$	ΔH_1°	$\Delta S_1^\circ \simeq 30$ e.u.
$(KM'Cl_{n+1}) = {}^1/_2(K_2Cl_2) + {}^1/_2(M_2Cl_{2n})$	ΔH_δ°	$\Delta S_\delta^\circ \simeq 0$
${}^1/_2(K_2Cl_{2n}) = (KCl)$	$\Delta H_2^\circ = 22.3$ kcal mole^{-1}	
	$\Delta S_2^\circ = 14.2$ e.u.	
${}^1/_2(M_2Cl_{2n}) = (MCl_n)$	${}^1/_2\Delta H_{dim}^\circ = \Delta H_1^\circ - \Delta H_\delta^\circ - \Delta H_2^\circ$	
	${}^1/_2\Delta S_{dim}^\circ = \Delta S_1^\circ - \Delta S_2^\circ$	

On the basis of many comparisons in this work[6] values for ΔH_δ° from 14 to 22 kcal mole^{-1} are proposed, depending on the position of the element in the Periodic System. The energies of dimerisation for the chlorides calculated in that work agree satisfactorily with the available experimental data. For the dimerisation of the alkaline earth metal chlorides, processes which have not been studied, the following values for the energies have been evaluated: 45, 50, and 42 kcal × × mole^{-1} for $CaCl_2$, $SrCl_2$, and $BaCl_2$ respectively. Although these values are rather high, and this shows the stability of the dimeric molecules in the vapour, they do not contradict the well-known monomeric nature of calcium, strontium, and barium chlorides in the vapour. The fact is that in the range 1000–1500°K the vapour pressure of the alkaline earth metal chlorides is low (1–20 mmHg) and consequently the degree of association should also be small.

In the general form the expression for the degree of association of the species in the saturated vapour has the form[6]:

$$\alpha = \frac{1}{1 + 0.5\exp\left(-\frac{\Delta S^\circ_{sub} - \Delta S^\circ_{diss.dim}}{R}\right)\exp\left(\frac{\Delta H^\circ_{sub} - \Delta H^\circ_{diss.dim}}{RT}\right)},$$

from which it follows that the value of α is determined by the difference in the thermodynamic characteristics of sublimation (vaporisation) and the dissociation of the dimer and also by the temperature.

This means that the degree of association in the vapour is determined not solely by the characteristics of stability of the dimeric molecules. High values of ΔH° for the dissociation of dimers can go with very low degrees of association in the vapour and contrariwise. Examples of this are $FeCl_3$ and KCl. The former is almost completely dimerised in the vapour at the boiling point ($\alpha = 1$) whereas the latter has the value $\alpha \simeq 0.04$ at the same temperature, although the dimer Fe_2Cl_6 is less stable than K_2Cl_2 ($\Delta H^\circ_{diss.dim}$ = 31.6 and 44.5 kcal mole^{-1} respectively)[14,79].

It follows that instances when experiment does not disclose dimeric (or polymeric) molecules cannot always be proof of the instability of the latter, but is evidence only of the insufficient sensitivity of the method. In this respect the following example is instructive. An investigation of the vapour-phase chlorides of the rare-earth elements by electron diffraction[77] showed that they are monomers but in a mass spectrometric analysis of the vapour of the same chlorides[81] ions of the $Ln_2Cl_5^+$ type are observed, that is, fragments of a dimeric molecule.

‡ Strictly "enthalpy of dimerisation" (Ed. of Translation).

Judging by the thermodynamic characteristics of the dissociation:

$$(Ln_2Cl_6) = 2(LnCl_3) \quad \begin{matrix}\Delta H^\circ_{1000} \simeq 40 \text{ kcal mole}^{-1} \\ \Delta S^\circ_{1000} \simeq 30 \text{ e.u.}\end{matrix}$$

the dimeric molecules are completely stable, but since at 1000°K the vapour pressure of the r.e.e. chlorides is very low ($\sim 10^{-3}$ mmHg) the vapour contains only 0.1–1% of dimeric molecules and therefore it is impossible to detect them by electron diffraction.

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As the above material shows, the contemporary state of the problem of vapour-phase complex halides is to a significant degree on the level of the accumulation of facts. Attempts to generalise and make recommendations run into difficulties on account of the absence of information about structures and the nature of the bonds in these compounds, even without mentioning the inadequate thermodynamic study and the complete absence of data on the kinetics of the formation and breakdown of complex vapour-phase species. However, although the facts are few, their treatment is already of practical and theoretical importance.

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MECHANISM OF REACTIONS OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

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I. INTRODUCTION

Depending on the electronic nature of the breaking of old bonds and the formation of new bonds, all substitutions can be classified into three groups: nucleophilic substitutions S_N, electrophilic substitutions, S_E, and homolytic substitutions S_R.

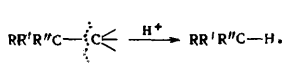
In distinction from the nucleophilic and homolytic substitutions, which have been well studied, the mechanism of electrophilic substitution at a saturated carbon atom was a blind spot in organic chemistry even a decade ago. However, the intensity of the study of the mechanism of this type of reaction is now increasing rapidly.

The reason for this, in addition to interest in the S_E reactions for their own sake, is apparently that as a result of discussion between Ingold and Sven† ideas about the mechanism of nucleophilic substitutions, and in particular S_N1 reactions, were greatly complicated. In this connection there was a natural tendency for a series of great chemists to switch to a study of the mechanism of electrophilic substitutions to try to transfer the regularities thus found to the mechanism of nucleophilic substitution.

To compare ideas about the mechanism of S_E reactions, the first essential is a combined study of their stereochemistry and kinetics, as it is in many other instances.

In distinction from nucleophilic and homolytic substitutions, here above all arises the difficulty of selecting suitable subjects for study, especially as regards stereochemistry. Few such subjects are known as yet.

From 1955 until now Cram (a survey of his work has appeared[3]) has completed a great series of works on the study of the stereochemistry of the reaction for the breaking of a carbon–carbon bond under the action of substances which are proton donors:



As a result interesting facts were obtained on the chemistry of carbanions but in most instances Cram was unable to study the kinetics of the reaction.

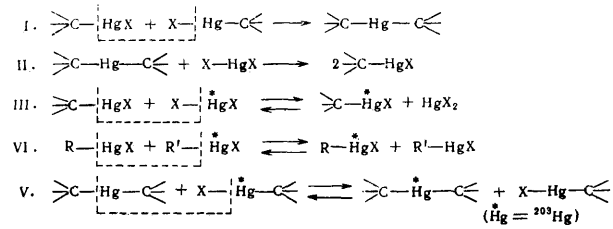
Evidently the most suitable subjects for studying the mechanism of electrophilic substitution at a saturated carbon atom should be organometallic compounds, owing to the definite nature of the polarisation of the metal–carbon bond:

$$^{(+)}M-C^{(-)}.$$

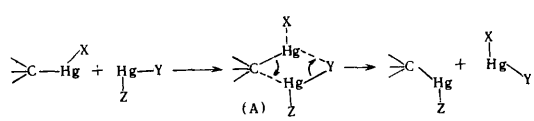
Of all the organometallic compounds, organomercury compounds are the most convenient: they are stable under ordinary conditions but sufficiently reactive, easily prepared, purified, and identified. Therefore, in recent years the most significant progress has been made in studying S_E reactions of organomercury compounds.

2. BIMOLECULAR ELECTROPHILIC SUBSTITUTION (S_E2) AT A SATURATED CARBON ATOM

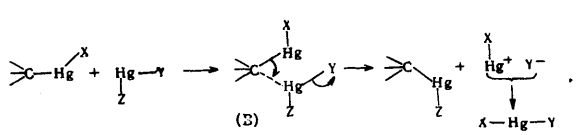
Study of the kinetics and stereochemistry of the electrophilic substitution at a saturated carbon atom of types I–V:



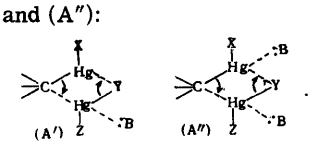
led to the conclusion that in non-polar and low-polar solvents the above reactions pass through the stage of formation of a cyclic four-membered transition state of type (A)[4–7]‡:



(I) X = Y = Hal, Z = Alk; (II) X = Alk, Y = Z = Hal; (III) X = Y = Z = Hal; (IV) Z = Alk, X = Y = Hal; (V) X = = Z = Alk, Y = Hal. The bases for taking such a structure of the transition state are: bimolecular reactions (kinetics of the second order overall and first order with respect to each of the components) proceed with strict retention of the stereochemical configuration, that is, the newly entering metal atom strictly takes the place of that leaving[8–11]; finally, the open transition state of type (B) is improbable in non-polar and low-polar solvents, because it would lead to the intermediate formation of the ions§ HgX^+ and Y^+:



Naturally, with a solvent in whose molecules there are atoms with unshared electron pairs (pyridine, dimethylformamide, ammonia) one or both of the mercury atoms in the transition state should be solvated or even bound by a coordination bond with solvent molecules — the transition states (A′) and (A″):



† The problems have been reviewed.[1,2]

‡ S_E2 reactions which proceed through a stage of a cyclic transition state are often denoted by the symbol S_Ei.

§ It is quite probable that S_E2 reactions proceed through transition state (B) in polar solvents.[12,13]

For the reactions of one-alkyl isotopic exchange (III) and symmetrisation (I) such coordination has been shown experimentally. Thus the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with mercury(II) bromide in dimethylformamide is really the reaction of R–Hg–X and a complex of HgX_2 with dimethylformamide[14]:

$$R{-}HgX + \overset{*}{H}gX_2\cdot C_3H_7ON \rightleftarrows R{-}\overset{*}{H}gX + HgX_2\cdot C_3H_7ON .$$

Undoubtedly, when the reaction is carried out in pyridine[6,15] the active reagent is $HgX_2.C_5H_5N$, not free HgX_2. The symmetrisation of the same substance under the action of ammonia in chloroform:

$$2R{-}HgX + 2NH_3 \rightarrow R_2Hg + HgX_2\cdot(NH_3)_2,$$

proceeds through the preliminary stage of the formation of a complex of the organomercury compound with ammonia, evidently by scheme 1¶:

Scheme 1

(a) $R{-}HgX + NH_3 \overset{\text{fast}}{\rightleftarrows} R{-}HgX\cdot NH_3$

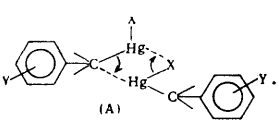
(b) $2R{-}HgX\cdot NH_3 \xrightarrow{\text{slow}} R_2Hg + HgX_2\cdot(NH_3)_2\}\ S_E2.$

Here the S_E2 reaction proceeds through the transition state of type (A").

It is easy to see, however, that general conclusions about the mechanism of the S_E2 reactions at a saturated carbon atom, made in considering the transition state (A). whether or not involving solvation or coordination of mercury atoms, will be identical†, because the transition state (A) will not differ significantly from transition state (A").

The main feature of all these transition states is a four-membered ring (A). This very feature is also responsible for symmetrisation with reactions (II)–(V) and determines the corresponding theoretical conclusions made on the basis of an independent study of S_E2 reactions of all five types. Therefore in judging subsequently the characteristic features of the symmetrisation we will consider for clarity a four-membered cyclic transition state (A), so to speak, "in the pure aspect", having, of course, in mind, that in reality either one or both of the mercury atoms are coordinated to molecules of ammonia.

In studying the influence of structural factors on the rate of symmetrisation of a series of substituted α-ethoxycarbonylbenzylmercury(II) bromides it was concluded that in transition state (A) the breaking of the old C–Hg bond plays a more important part than the formation of the new one[5,6]:



(A)

The values of the rate constants for second-order reactions k_2 are given in Table 1.

The influence of substituents Y on this reaction obeys the Hammett equation. Clearly the order of the influence of the substituents is reversed in comparison with typical

TABLE 1.

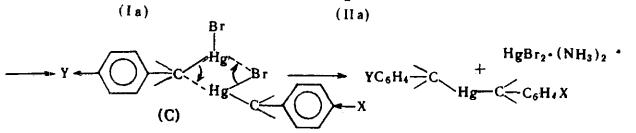
Y	*p*-NO_2	*p*-I	*p*-Br	*m*-Br	*o*-Br	*p*-Cl	*p*-F	H	*p*-CH_3	*m*-CH_3	*o*-CH_3	*p*-C_2H_5	*p*-$(CH_3)_2CH$	*p*-$(CH_3)_3C$
k_2, ml mole^{-1} s^{-1}	17 730	670	540	1445	426	470	148	110	34	71	32	41	42	28

* The constant k_2 was calculated assuming that Hammett's equation is applicable to this series (ρ = 2.85).

S_E2 reactions‡. This feature can be interpreted in the same way, that in consequence of the specific properties of the given organomercury compounds used (high lability of the C–Hg bond), the S_E2 reaction being studied is in the boundary region close to the region of S_E1 reactions unknown until recently (see p. 167).

Since in the transition state (A) not only the old C–Hg bond but also the old Hg–Br bond is broken it is natural to assume that such a type of transition state will be attained more easily for reactions between molecules of different types (Ia) and (IIa):

$$\underset{\text{(Ia)}}{YC_6H_4CH(HgBr)COOR} + \underset{\text{(IIa)}}{XC_6H_4CH(HgBr)COOR} \xrightarrow{2NH_3}$$



(C)

The electron-withdrawing substituent Y should facilitate the breaking of the old C–Hg bond in transition state (C), and the electron-donating substituent X, should facilitate the breaking of the old Hg–Br bond. Therefore such a type of "cosymmetrisation" should be faster than the symmetrisation of either of the two pure substances. Experiment completely confirmed this. Finally, by use of radioactive mercury ^{203}Hg it was shown[24] that a mercury atom from the original molecule (Ia) with a substituent Y preferentially transfers into the complex $HgBr_2.(NH_3)_2$ but an atom of mercury from molecule (IIa) with a substituent X goes into the organomercury compound formed, as can be predicted by starting from the transition state (C):

$$\underset{\text{(Ia)}}{YC_6H_4{-}\overset{COOC_2H_5}{\overset{|}{C}}H{-}\overset{*}{H}g{-}Br} + \underset{\text{(IIa)}}{XC_6H_4{-}\overset{COOC_2H_5}{\overset{|}{C}}H{-}Hg{-}Br} \xrightarrow{2NH_3}$$

$$\longrightarrow YC_6H_4{-}\overset{COOC_2H_5}{\overset{|}{C}}H{-}Hg{-}\overset{COOC_2H_5}{\overset{|}{C}}H{-}C_6H_4X + \overset{*}{H}gBr_2\cdot(NH_3)_2$$

where Y = Br, X = H; Y = H, X = CH_3; Y = Br, X = CH_3.

Hence the above cyclic transition state in the S_E2 reactions of organomercury compounds can now be considered adequately proved§.

Note that the work of Dessy and coworkers[28] has suggested the possibility of a more complex transition state in S_E2 reactions at a saturated carbon atom than that proposed by Reutov[4-7] and Ingold[29]. However Dessy's work was not confirmed when checked[30].

¶ The basis for the scheme is given and discussed elsewhere.[16-20]

† Jensen and Rickborn's views on this[20,21] are based on a misunderstanding and are erroneous (see Reutov[22]).

‡ Note that such an "anomalous" influence of substituents is observed in the reaction of esters of α-bromomercuriarylacetic acids with I_2/CdI_2 in toluene.[23]

§ The field of the reactions of organometallic compounds proceeding through an analogous cyclic transitional state, which has been studied, includes some bimolecular electrophilic substitutions of hydrogen, halogen, and metal for metal at saturated, alkene, and aromatic carbon atoms.[18,25-27]

3. SYMMETRISATION OF ORGANOMERCURY COMPOUNDS WITH THE AID OF DIPHENYLMERCURY

Diphenylmercury was proposed[31] as a symmetrising agent for organomercury compounds with a labile C–Hg bond:

$$(C_6H_5)_2Hg + 2R{-}HgX \rightarrow R_2Hg + 2C_6H_5{-}HgX\downarrow,$$

where R = CH_3COCH_2, ClCH=CH, or $ArCH{=}COOC_2H_5$.

Three possible reaction schemes were considered:

Scheme 1

(a) $2R{-}HgX \rightleftarrows R_2Hg + HgX_2$
(b) $(C_6H_5)_2Hg + HgX_2 \rightarrow 2C_6H_5{-}HgX\downarrow$

Scheme 2

(a) $R{-}HgX + (C_6H_5)_2Hg \rightarrow C_6H_5{-}Hg{-}R + C_6H_5HgX\downarrow$
(b) $C_6H_5{-}Hg{-}R + R{-}HgX \rightarrow R_2Hg + C_6H_5HgX\downarrow$

Scheme 3

(a) $R{-}HgX + (C_6H_5)_2Hg \rightarrow C_6H_5{-}Hg{-}R + C_6H_5HgX\downarrow$
(b) $2C_6H_5{-}Hg{-}R \rightleftarrows (C_6H_5)_2Hg + R_2Hg.$

Jensen and Miller[32] thought the last two schemes equally probable. However, on using esters of α-bromomercuriarylacetic acids (R = $ArCHCOOC_2H_5$) labelled with ^{203}Hg it was shown[33] that the reaction mechanism corresponds to scheme 2, but not 1 or 3.

It is easy to see (scheme 2) that both stages of the reaction are completely analogous to the three-alkyl isotopic exchange of organomercury compounds discovered earlier[10,11,34].

4. STEREOCHEMISTRY OF THE S_E2 REACTIONS

All the S_E2 reactions at a saturated carbon atom yet studied by the example of organomercury compounds proceed with strict retention of the stereochemical configuration.

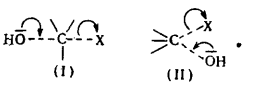
Examples of this are the symmetrisations[8,9] considered above, the three-alkyl isotopic exchange (p. 164, reaction of type V) discovered by Reutov and coworkers[10,11] and somewhat later independently by Ingold and coworkers[34].

Such a reaction of symmetrical organomercury compounds with a mercury halide (p. 164, reaction II) was studied by Ingold and coworkers[35] and by some others.

The S_E2 rule has been formulated[6], according to which bimolecular electrophilic substitutions at a saturated carbon atom proceed with retention of the configuration.

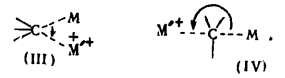
It is important to attempt to answer the following natural question: is the S_E2 rule, which has been developed on the basis of a study of reactivity of only organomercury compounds, generally applicable?

The inversion of the configuration in S_N2 reactions at a saturated carbon atom is known to be due to the fact that of the two possible transition states (I) and (II), the first is energetically more favourable.



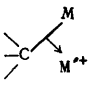
(I) (II)

In a similar fashion, of the two possible transition states (III) and (IV) in S_E2 reactions, state (III) should apparently be more preferable in energetic respects — without even speaking about the stabilisation which is often possible on account of the formation of type (A) rings (see p. 164):



(III) (IV)

By analogy with π-complexes it could be suggested that transition state (III) comes about from the preliminary formation of a σ-complex (V):



(V)

However, unlike the π-complexes, there is still no experimental proof of the existence of such σ-complexes. On the other hand it is difficult to oppose the hypothesis that the formation of transition state (III) precedes the attack by the cation on the C–M bond in the sense of a hypothetical σ-complex (V).

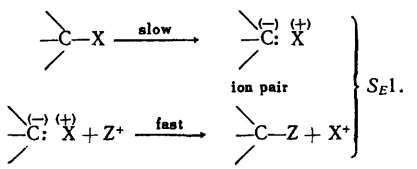
As for spatial factors, they are not very favourable for the retention of configuration for organomercury compounds because of the large covalent and van-der-Waals radii of the mercury atom. Hence the spatial factor which hinders reaching transition state (III) probably cannot change the stereochemical result even for extremely large M and M′.

On the basis of the above it can be suggested that the rule of the retention of configuration in S_E2 reactions can be of a rather general character¶.

5. UNIMOLECULAR ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

Of the four possible mechanisms of heterolytic substitution at a saturated carbon atom (S_N2, S_N1, S_E2, and S_E1) the S_E1 type remained undiscovered until the most recent time.

In the general form the S_E1 mechanism can be expressed as follows:



In the first, slow stage the reaction proceeds by ionisation of the C–X bond with formation of a carbanion (part of an ion pair). In the second, rapid stage of the reaction the ion pair reacts with the electrophilic reagent (Z^+), forming the final compound.

The hope of realising the S_E1 mechanism appeared in connection with the results of stereochemistry and kinetics of symmetrisation of esters of α-bromomercuriarylacetic acids under the action of ammonia.

As noted above, the nature of the influence of the structural factors on the rate of the S_E2 reactions being considered showed that in the transition state (A) the breaking of the old C–Hg bond played a more important part than the formation of the new bond[4,6].

¶ A known instance of the inversion of configuration in an S_E2 reaction of 5-norbornene-2-boronic acid with $HgCl_2$ is explained by the exchange of the boronic acid residue for the HgCl residue being a transannular (and not the usual) electrophilic substitution[36]. Winstein[37] described a similar example.

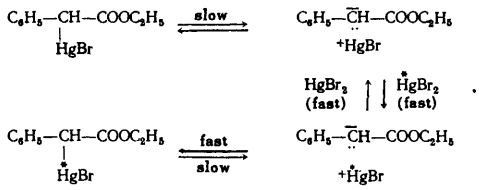
This conclusion, which is unusual for bimolecular reactions, shows that this reaction is close to the boundary region between S_E2 and S_E1 reactions (for the latter, as stated earlier, the stage of ionisation of the old bond is the most important stage)†.

It can be hoped that when the reactions (for the same esters of α-bromomercuriarylacetic acids) are carried out in a solvent with a high ionising ability the S_E1 mechanism will be effected.

Such an attempt, which was crowned with success, was made for the isotopic exchange:

$$RR'R''C{-}HgBr + {}^{*}HgBr_2 \rightleftarrows RR'R''C{-}{}^{*}HgBr + HgBr_2 .$$

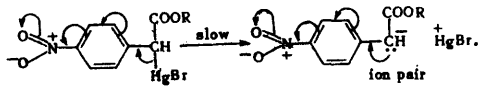
The isotopic exchange in pyridine, dimethylformamide, and ethanol is an S_E2 reaction[15,16]. However, when dimethyl sulphoxide (DMSO), which exhibits high ionising ability, is used as the solvent the kinetics and mechanism of the reaction immediately change. The reaction is first order with respect to the α-bromomercuriarylacetate ester and zeroth-order to the mercury(II) bromide. Hence an S_E1 type of reaction was discovered for the first time[38].



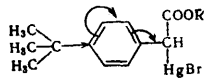
The influence of substituents X in the *para*-position of the benzene ring on the rate of isotopic exchange was studied. The experimental results for substituted α-ethoxycarbonylbenzylmercury(II) bromides at 30° are given in Table 2.

Electron-donating substituents (t-butyl) decrease, but electron-accepting substituents (I, NO_2) increase, the rate of reaction.

Such an order of influence agrees with the predictions about the S_E1 mechanism: electronegative substituents should facilitate breaking of the carbon–mercury bond and stabilise the carbanion, which is formed (as part of an ion pair) as a result of the slow stage of ionisation of the organomercury compound:

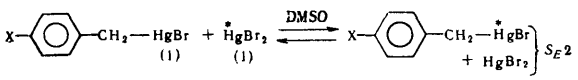


The action of the electropositive substituents will be opposing:



(hence the slow rate of ionisation and consequently of the overall reaction as a whole)‡.

In studying the isotopic exchange in DMSO of benzyl organomercury compounds (less reactive in S_E reactions than esters of α-carboxybenzylmercury(II) bromides) it was found[44] that the reaction takes place by a bimolecular, not a unimolecular, mechanism:



where X = $(CH_3)_2CH$, CH_3, H, Cl, or F, that is, just as when quinoline is used as solvent[45]§.

TABLE 2.

Compounds p-XC_6H_4–CH(HgBr)–$COOC_2H_5$	X		
	$(CH_3)_3C$	I	NO_2
$\frac{k_X}{k_H}$ (DMSO, 30°)	0.71	1.31	4.04

† Note that esters of α-bromomercuriarylacetic acids, like other α-mercurated oxo-compounds, exhibit an extremely labile C–Hg bond, and tend to ionise to a greater extent than the usual alkyl and aryl organomercury compounds.

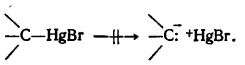
‡ Ingold and coworkers[39] repeated the work of Reutov and coworkers[38,40] and confirmed completely the results about the S_E1 mechanism in the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with $^{203}HgBr_2$ in DMSO. In addition, they could not reproduce the results of our work[40] in 70% aqueous dioxan, where kinetics of the first order with respect to the organomercury compound and zeroth order in $^{203}HgBr_2$ were observed also (and consequently, an S_E1 mechanism). According to Ingold's results, which he himself considers preliminary, overall second-order kinetics was observed (first in R–HgX and first in $^{203}HgX_2$). Recently Reutov and Sokolov again repeated the work with 70% aqueous dioxan and reproduced their experimental results published earlier[40,41]. The reason for the above differences in the work with dioxan are still not completely clear to the two groups of investigators. This problem, however, no longer is of principal significance, since both Reutov and Ingold[42,43], "agree qualitatively and quantitatively in principle: the S_E1 mechanism is clear in studying the isotopic exchange of α-ethoxycarbonylbenzylmercury(II) bromide with $HgBr_2$ in DMSO" [Ingold's actual words[43] are: "We are agreed, qualitatively and quantitatively, about the fact of main interest; namely that, in anhydrous DMSO, the substitution in α-ethoxycarbonylbenzylmercury(II) bromide by $^{*}HgBr_2$ is of first order in the organo-mercuric salt and of zeroth order in the mercuric salt and hence must have the S_E1 mechanism" (Ed. of Translation)].

§ It is interesting that allylmercury(II) bromide reacts extremely rapidly with $HgBr_2$:

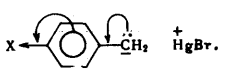
$$CH_2{=}CH{-}CH_2{-}HgBr + {}^{*}HgBr_2 \rightleftarrows CH_2{=}CH{-}CH_2{-}{}^{*}HgBr + HgBr_2 .$$

The isotopic equilibrium is established almost instantaneously at room temperature in various solvents: DMSO, quinoline, acetone, toluene.

Evidently, despite the high ionising ability of DMSO it is here insufficient to ionise the strong C–Hg bond to form an ion pair:



It is natural to assume that the probability of the existence of an S_E1 mechanism of this reaction in DMSO should rise when the carbanion formed as a result of the ionisation exhibits a greater stability owing to the delocalisation of the negative charge, for example, due to structural factors:

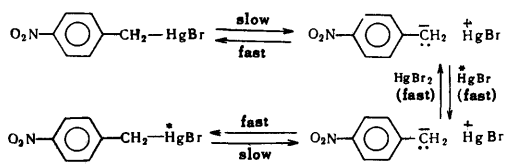


The most suitable subject for the accomplishment of an S_E1 mechanism should be substituted benzylmercury(II) halides with strongly electronegative substituents in the benzene ring. Experimental verification confirmed this prediction.

The kinetics of the isotopic exchange of *p*-nitrobenzylmercury(II) bromide with radioactive mercury(II) bromide in DMSO was studied. As expected, the reaction was of first order overall (first order in organomercury compound and zeroth order to mercury bromide).

Hence an S_E1 reaction of the type being considered was achieved also for benzyl systems, wholly directed by using structural factors and the ionising ability of the solvent[46].

The reaction mechanism can be expressed as follows:



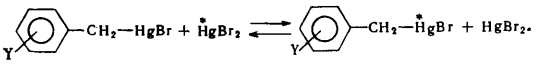
The influence of the halogen X in the compounds $YC_6H_4-CH_2-Hg-X$ on the rate of the S_E1 and S_E2 reactions of isotopic exchange has been studied. It was found that the influence of X is the same in the two instances. The rate of isotopic exchange rises in the sequence: Cl < Br < I.

Such a regularity is understandable, because the more electronegative halogen by induction influence should decrease the effective negative charge on the carbon atom and retard the S_E2 reaction all the same. On the other hand a more electronegative halogen should hinder heterolytic breaking of the C–Hg bond to form a carbanion (retardation of the S_E1 reaction).

Ingold and coworkers[47] described one more example of S_E1 reaction: interaction of di-s-butylmercury with diethylallyl bromide in dimethylformamide, which takes place with racemisation. However, the conclusion about an S_E1 mechanism here seemed erroneous, since no allowance was made in the work for oxidation of the organomercury compound proceeding under the action of atmospheric oxygen[78].

6. ANIONIC CATALYSIS OF ONE-ALKYL ISOTOPIC EXCHANGE

The isotopic exchange of benzylmercury(II) halides with $^{203}HgX_2$ seemed convenient for studying characteristic peculiarities of anionic catalysis discovered by Ingold and coworkers[48] for one-alkyl isotopic exchange:



As shown above, this isotopic exchange takes place in quinoline and dimethyl sulphoxide (with the exception of when Y = NO_2) as an S_E2 reaction:

k_2 (quinoline) = 0.13 litre mole^{-1}h^{-1}; k_2(DMSO) = 0.37 litre mole^{-1}h^{-1}.

In the presence of potassium bromide the isotopic exchange is appreciably faster. For example, at concentrations $[HgBr_2] = [R-HgBr] = 0.06$ M the rate constant of the reaction¶ rises in the following manner as [KBr] is increased[44]:

[KBr], M	0	0.06	0.12	0.18
10^2k_2, litre mole^{-1}h^{-1}	37	148	1444	2139.

The influence of the nature of substituent Y situated in the *para*-position of the benzene ring is opposite for the unactivated reaction and for a reaction catalysed by additions of KBr[44]. Table 3 gives the half-exchange periods $\tau^{1/2}$ in minutes for various $YC_6H_4-CH_2-HgBr$ at [KBr] = = 0, 0.09, and 0.12 M (in DMSO at 70°).

From Table 3 it is evident that in a non-catalysed S_E2 reaction the substituents are arranged in the following sequence as regards accelerating influence:

Cl, F < H < CH_3, $(CH_3)_2CH$.

With isotopic exchange in the presence of KBr the picture changes sharply. In addition to strong acceleration of the reaction there is a change in the influence of the substituent, to the contrary order[44]:

$(CH_3)_2CH < CH_3$, H < F < Cl.

The influence of additions of KBr can be explained by the complexes $HgBr_3^-$ and $R-HgBr_2^-$ being formed in the system:

[(a) $HgBr_2 + Br^- \rightleftarrows HgBr_3^-$; (b) $RHgBr + Br^- \rightleftarrows RHgBr_2^-$],

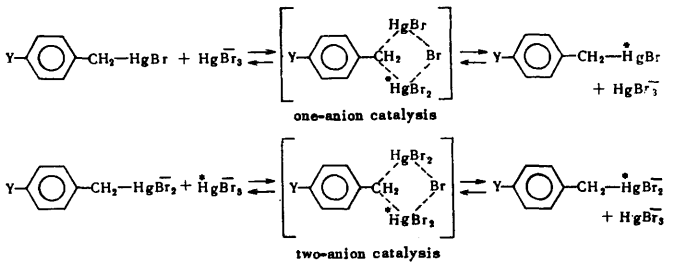
and these complexes are capable of undergoing isotopic exchange. Evidently the second complex should be formed with greater difficulty (that is, at higher KBr concentrations).

TABLE 3.

[KBr], M	$[HgBr_2]$, M	$[YC_6H_4CH_2HgBr]$, M	$\tau^{1/2}$, min for Y =				
			Cl	F	H	CH_3	$(CH_3)_2CH$
0.00	0.06	0.06	1140	1140	1020	780	780
0.09	0.06	0.06	24	35	45	45	50
0.12	0.06	0.06	10	18	25	25	30

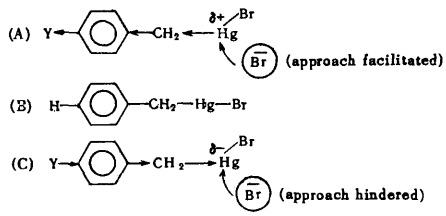
¶ At high potassium bromide concentrations (for example, $[KBr]/[HgBr_2] \geq 2$) k_2 is not maintained sufficiently satisfactorily. This can be explained either by a salt effect or by the fact at relatively high KBr concentrations the reaction can proceed in parallel by the S_E2 and S_E1 mechanisms.

Hence for this isotopic exchange it is evidently necessary to allow for there being two parallel reactions:



If two-anion catalysis is stronger than one-anion catalysis, then the rate of reaction should depend directly on the concentration of the complex $R-HgBr_2^-$. It is evident that substituent Y should affect the ease of formation and consequently also the concentration of this complex.

From this point of view it is understandable why in isotopic exchange catalysed by KBr there is the reverse order of influence of substituents in comparison with the non-catalytic reaction. Naturally the electronegative substituents, which draw off the electron density from the mercury atom, should facilitate the formation of a complex with a bromide anion (in comparison with unsubstituted benzylmercury bromide) (see A):



On the other hand, for the electron-donating substituents the formation of a covalent bond of the bromide anion with a mercury atom should be hindered (see B)†.

For isotopic exchange by mechanism S_E1 in the presence of KBr it would be expected that of the two complex formation processes (a) and (b):

$$\text{(a)}\quad HgBr_2 + Br^- \rightleftharpoons HgBr_3^-$$
$$\text{(b)}\quad RHgBr + Br^- \rightleftharpoons RHgBr_2^-$$

only the second, (b), will affect the rate of the reaction, because the ionisation of the C–Hg and $R-HgBr_2^-$ bonds should proceed more readily than in R–HgBr.

The S_E1 mechanism, which is catalysed by KBr, can be represented as follows:

$$R-HgBr + Br^- \xrightarrow{\text{fast}} R-HgBr_2^-$$
$$R-HgBr_2^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \bar{R}: \quad HgBr_2$$
$$HgBr_2\ (\text{fast}) \uparrow\downarrow {}^*HgBr_2\ (\text{fast})$$
$$R-{}^*HgBr_2^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \bar{R}: \quad {}^*HgBr_2$$

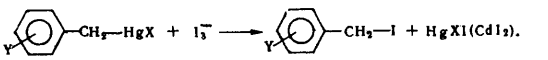
† In principle the possibility of the anion $HgBr_4^{2-}$ (instead of $R-HgBr_2^-$) also participating in two-anion catalysis must be considered. The results of a study[44] of the influence of substituents Y on the reaction rate support the anion $R-HgBr_2^-$, at least for the benzylmercury bromides mentioned above.

Experiment confirms[49] the above hypothesis of the effect on the reaction rate for only the process of formation of the complex $RHgBr_2^-$.

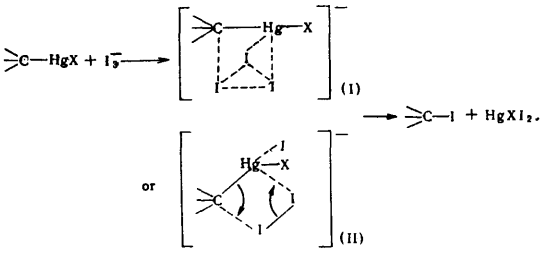
Study of the S_E1 reaction of isotopic exchange of *p*-nitro-benzylmercury(II) bromide with $^*HgBr_2$ in DMSO showed that the reaction rate changes significantly with the KBr concentration. The rate of exchange rises significantly even at KBr concentrations somewhat less than the $^*HgBr_2$ concentration. Thus at [KBr] = 0.05 M, ([$HgBr_2$] = 0.06 M, [RHgBr] = 0.03 M), the rate of exchange increases by a factor of 8. This fact evidently shows that even at KBr concentrations less than the $HgBr_2$ concentration the formation of $RHgBr_2^-$ in the system also takes place to some extent in addition to the formation of $HgBr_3^-$. Naturally a further rise in the KBr concentration rapidly increases the $RHgBr_2^-$ concentration, which should lead to a sharp acceleration of the reaction. At [KBr] = 0.09 M the initial isotopic exchange rate is 47 000 times greater than that in the absence of KBr.

7. HALODEMERCURATIONS

The reaction of benzylmercury halides with iodine in the presence of an excess of cadmium iodide is second-order overall (first with respect to each of the components) in methanol, ethanol, butanol, 70% aqueous dioxan, acetonitrile, dimethylformamide, and dimethylsulphoxide[50-52]. Proof was obtained that I_3^- participates in the reaction (compare Winstein and Traylor[53]):



This S_E2 reaction evidently proceeds through a transition state of type (I) or (II)[52]:



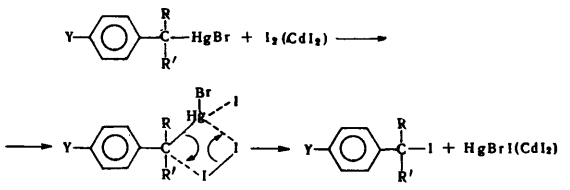
The influence of substituent Y in the benzene ring is shown in Table 4 (k_2 in litre mole^{-1} s^{-1}, in absolute methanol at 19°).

It was noted earlier that the nature of the influence of structural factors on the rate of symmetrisation of esters of α-bromomercuriarylacetic acids shows that in the cyclic four-membered transition state of type (A) the breaking of

TABLE 4.

Y	H	CH_3O	CH_3	F	Cl	Br	NO_2
para	—	8.33	1.93	0.84	0.71	—	instantaneous
meta	0.75	—	0.83	0.42	—	0.46	—
ortho	—	—	1.75	0.22	0.23	—	—

the old C–Hg bond is the determining factor. This conclusion is confirmed also for the reaction of α-bromomercuriarylacetic esters with iodine in the presence of cadmium iodide[23]. The reaction was studied in absolute toluene with additions of 1.5 vol.% methanol:



with R = $CO_2C_2H_5$, R′ = H.

The values of the rate constants for a second-order reaction given in Table 5 show that the sequence of the influence of substituents is here analogous to the sequence of the influence for the symmetrisation.

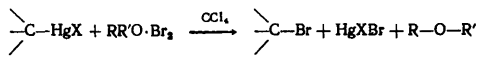
Halodemercuration is somewhat less sensitive to the influence of substitutents (ρ = 2.3) than symmetrisation.

Hence the S_E2 mechanism for the iodination of these compounds is also in a boundary region adjoining the region of reactions which take place by an S_E1 mechanism. This example is again evidence of the arbitrary nature of the division of mechanisms of substitutions into two extreme types.

The reaction of $Ar-CH_2-HgX$ with halogens in the presence of CdX_2 or NH_4X also are S_E2 reactions[54-58].

The reaction of benzylmercury(II) halides with iodine and bromine in the absence of CdX_2 in non-polar solvents (for example, in carbon tetrachloride) is photochemical‡ and proceeds by a radical-chain mechanisms[59,60]. However, small additions of H_2O, ROH, or R_2O in the reaction mixture (0.25 vol.%) alter the kinetics of the reaction of organomercury compounds with bromine (but not with iodine), and consequently also the mechanism itself[62]. For example, irradiation no longer affects the reaction rate. The kinetics of the reaction becomes second-order (first in each of the reagents).

It is natural to assume that this result is due to the formation of a complex of bromine with oxygen-containing molecules and the subsequent participation of this complex in an S_E2 reaction as a donor of electrophilic bromine§:



where R = R′ = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, R′ = H.

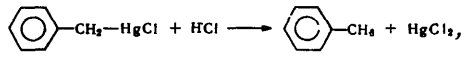
The rate constants for certain reactions in the presence of additions are given in Table 6.

Table 6 shows that the effect of oxygen-containing compounds on the reaction rate can be compared with the "coordination capacity" and electron-donor properties of these compounds.

8. PROTODEMERCURATION

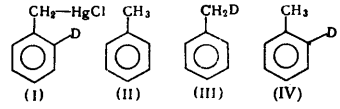
Some features of protodemercuration were studied by the example of benzyl organomercury compounds.

It was shown[63] that in alcohol and dioxan the reaction of benzylmercury chloride (BMC) with hydrogen chloride:



proceeds by an S_E2 mechanism.

In studying the reaction with DCl in dioxan under the conditions of pseudounimolecularity — $[BMC]_0$ = 0.25 M, [DCl] = 2.5 M — it was shown[64] that as the reaction proceeds substances (I), (II), (III), and (IV) appear in the reaction mixture¶:



After the reaction had finished, the reaction mixture naturally contained only compounds (II), (III), and (IV).

TABLE 5.

Y	p-NO_2	p-Br	p-I	p-Cl	p-F	H	m-CH_3	p-$(CH_3)_2CH$	p-$(CH_3)_3C$
k_2, litre mole^{-1} s^{-1}	615*	79.3	43.6	33.4	14.1	10.1	7.1	4.5	3.5

* The reaction is very fast when Y = NO_2, therefore here the constant was calculated assuming that Hammett's equation is applicable to this series.

TABLE 6.

Addition	H_2O	CH_3OH	C_2H_5OH	i-C_3H_7OH	n-C_4H_9OH
k_2, litre mole^{-1} s^{-1}	9.46	3.43	2.73	1.46	1.17

Addition	$(CH_3)_2O$	$(C_2H_5)_2O$	$(C_3H_7)_2O$	$(C_4H_9)_2O$
k_2, litre mole^{-1} s^{-1}	2.44	1.68	0.94	0.87

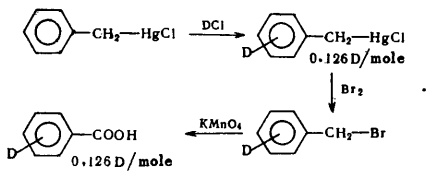
‡ The kinetics, stereochemistry, and mechanism of the homolytic replacement of a mercury atom (connected to a saturated carbon atom) by halogen have been studied by the example of $CH_3CH(HgBr)CH_2CH_3$ with bromine in CCl_4.[61]

§ The reason for the higher reactivity of the $R_2O.Br_2$ complexes in S_E2 reactions compared with Br_2 is given in the section "internal catalysis" (p. 171).

¶ Special experiments showed that the toluene formed does not undergo isotopic exchange with the DCl under the reaction conditions.

From the results given it follows first that BMC undergoes isotopic exchange with the DCl. This is evidently the deutero-exchange observed in organometallic compounds of the transition metals.

That the deuterium was present only in the BMC nucleus was shown as follows:



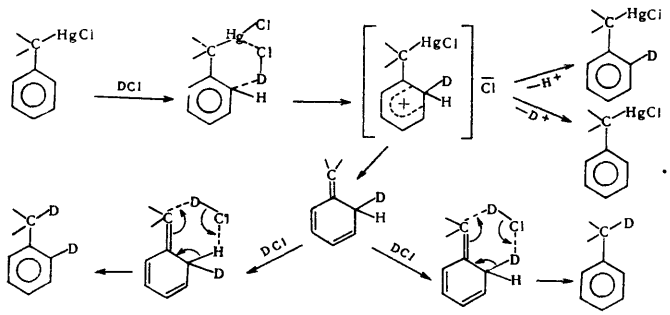
To determine the position of the deuterium in the BMC nucleus it was reduced with $LiAlH_4$ in toluene.



Infrared spectroscopy then showed that dueterium is in practice present only in the *ortho*-position (k_o/k_p = 25 : 1).

Table 7 gives the mass spectra of toluenes isolated at different amounts of conversion of BMC.

Taking all this into account, the mechanism of this rather complex reaction of BMC and DCl can evidently be rather satisfactorily represented by the following scheme [64]:



Bearing in mind the high lability of the C–Hg bond in the dibenzylmercury (DBM) molecules it could be calculated to provide the first example of an S_E1 reaction at a saturated carbon atom in the protolysis of organometallic compounds:

$$(C_6H_5{-}CH_2)_2Hg + HCl \longrightarrow C_6H_5{-}CH_3 + C_6H_5{-}CH_2{-}HgCl.$$

In fact it was shown that in DMSO the reaction proceeds by a first-order dependence and on replacing HCl by DCl the kinetic isotopic effect is absent [65]. This shows that with an overall first-order dependence the reaction has first-order dependence on DBM and zeroth-order on the acid.

TABLE 7.

BMC converted, %	Mass-spectrum of toluenes		
	d_2	d_1	d_0
25	36.4	51.2	12.4
50	36.2	50.2	13.5
70	37.9	48.0	14.0

The simplified mechanism can be represented by the scheme:

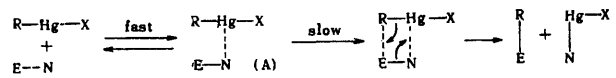
$$(a) \qquad (C_6H_5{-}CH_2)_2Hg \underset{}{\overset{\text{slow}}{\rightleftharpoons}} C_6H_5{-}\bar{C}H_2{:}\overset{+}{H}g{-}CH_2{-}C_6H_5$$

$$(b) \qquad \underset{\text{ion pair}}{C_6H_5{-}\bar{C}H_2{:}\overset{+}{H}g{-}CH_2{-}C_6H_5} + HCl \xrightarrow{\text{fast}} C_6H_5{-}CH_3 + Cl{-}Hg{-}CH_2{-}C_6H_5.$$

It is interesting that this reaction is also first-order in a series of other solvents: dimethylformamide, aqueous (5%) acetonitrile, tetrahydrofuran, butanol. The probable reason is the high lability of the C–Hg bond and also the formation in the reaction of a rather stable ion pair. Some features of the reaction remain inexplicable, for example, the rise in the rate constant k_1 with increase in the HCl concentration.

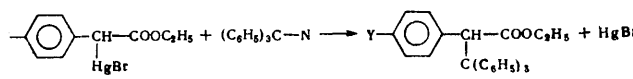
9. "INTERNAL CATALYSIS" IN S_E REACTIONS OF ORGANOMERCURY COMPOUNDS

In all S_E reactions of non-symmetrical organomercury compounds there is acceleration under the action of nucleophilic catalysts. Nucleophilic catalysis, which can be regarded as "external", has been mentioned above (the catalysis of isotopic exchange of organomercury compounds with bases, anionic catalysis, etc.). However, in many instances the catalytic action is connected with the preliminary formation of the complex R–HgX with E–N† of type (A), evidently in the pre-kinetic stage of the reaction. This can be termed "internal nucleophilic catalysis" or "internal nucleophilic assistance". Only after the formation of complex (A) is there the slow stage of the reaction — the formation of a new C–E bond:



The idea of "internal nucleophilic catalysis" in bimolecular electrophilic substitutions has been developed in several papers [66–69].

For example, the mechanism of the triphenylmethylation of ethyl α-bromomercuriarylacetates in dichloroethane has been studied:



where N = Br^-, $HgBr_3^-$, $HgBr_3^-$, ClO_6^-, $SnHal_6^-$.

When N = ClO_4^- there is not reaction, since the formation of a complex of type (A) is impossible. Reaction also does not occur with the strongly ionised compound $2(C_6H_5)_3C^+SnHal_6^{2-}$. The use of a weaker Lewis acid — mercury(II) bromide — even allows the alkylation to be carried out — by the complex $(C_6H_5)_3C^{\delta+}\ldots HgBr_3^{\delta-}$ — although the reaction is slower than for $(C_6H_5)_3C$–Br itself; with the latter it was shown spectrophotometrically that the reaction proceeds through the intermediate formation of the complex $RHgBr.(C_6H_5)_3CBr$.

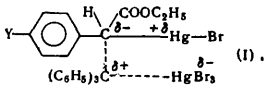
Apparently, in the above reactions the structures of the transitional compounds are different, which is confirmed by the diffferent influence of the substituents Y in the *para*-position of the benzene ring of the organomercury

† E denotes the electrophilic and N the nucleophilic, part of the molecule.

compound. Thus the reaction of mercurated ester with $(C_6H_5)CBr.HgBr_2$ is accelerated by electron-donating and retarded by electron-accepting substituents:

$$C_3H_7,\ C_2H_5 > C_6H_5 > H > F > Cl > Br > I > NO_2.$$

This is evidently connected with the significance of electrophilic attack on a carbon atom — transition state (I):

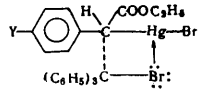


(I).

In the reaction of organomercury compounds with trityl bromide itself the influence of substituents Y is the reverse:

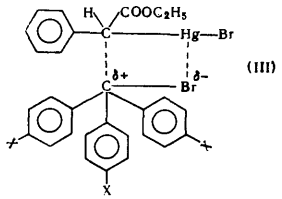
$$NO_2 > Hal > H > Alk.$$

The inversion of the influence of the substituents is evidently due to the influence on the reaction rate of the strength of the bond formed between the bromine and the mercury atom — transition state (II). Here it is possible that the determining factor will be the breaking of the old carbon–mercury bond, and not the formation of the new carbon–carbon bond, that is, the reaction mechanism approximates to the S_E1 type:



(II).

The fact that reaction does not occur when completely ionic compounds are used — for example, $(C_6H_5)_3C^+ClO_4^-$ — shows that in any alkylations of the type being considered one can scarcely expect realisation of a completely open structure of transition state (I) and that some fraction of coordination of $HgBr_3^{\delta-}$ with the mercury atom should occur, although less than for structure (II). That both factors — electrophilic attack at a carbon atom and nucleophilic coordination with the mercury atom — are important is also demonstrated by the influence of substituent X in the molecule of the electrophilic agent — transition state (III):



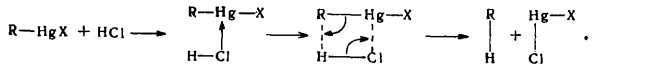
(III)

where X = CH_3, H, NO_2.

For example, the alkylation rate decreases on going from trityl bromide to tritolylmethyl bromide, that is, on reducing the positive effective charge on the carbon atom. However, a decrease in the effective negative charge on the bromine atom of the triarylmethyl bromide also hinders reaction. It was shown that tri-(*p*-nitrophenyl)methyl bromide, in which the carbon–bromine bond is more covalent than in trityl bromide generally does not alkylate a mercurated ester. Hence for trityl bromide there is an optimal combination of conditions which is responsible for the good alkylating ability of this substance. These results are good illustrations of the necessity for nucleophilic coordination in reactions of organomercury compounds‡.

An analogous regularity can be demonstrated by the example of the protolysis of organomercury compounds.

Reutov and coworkers [63] and Dessy and coworkers [71] showed that the rate of protolysis of organomercury compounds by hydrogen chloride decreases on raising the concentration of water in the solvent. This phenomenon is connected with the fact that at low water concentrations a rise in its concentration is accompanied by an increase in the solvation of HCl and its deactivation, but at higher water concentrations there is a simultaneous ionisation of the HCl, which also hinders the reaction. In addition to the other arguments (the absence of reaction with strong acids incapable of coordination with mercury, for example, $HClO_4$), this observation confirms the hypothesis that the reactant is not the solvated proton but the molecular form HCl, most probably its ion pair. In this it is possible that the nucleophilic coordination of chlorine with mercury occurs in the pre-kinetic stage and then is accompanied by electrophilic attack of hydrogen on carbon:



Naturally, as a result of this, a cyclic transition state is realised in the reaction. Possibly the formation of such a structure of a transition state is an important factor facilitating the strict retention of the stereochemical configuration in reactions of the S_E2 type.

It can be hoped that the conception of internal nucleophilic association will be quite helpful in organoelemental chemistry. Even now much of what was incomprehensible earlier has received a simple and natural explanation§ from the standpoint of this conception.

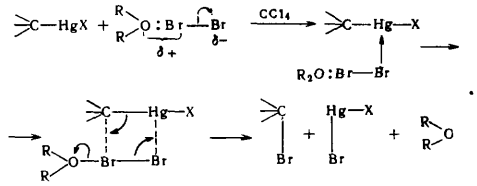
For example, it was not understood earlier why the complexes of bromine with ethers $R_2O.Br_2$ are more effective reagents in S_E2 reactions with organomercury compounds than free [62]bromine (see p. 170).

Taking into account the necessity for internal nucleophilic association this is easy to understand: in the complex $R_2O.Br_2$ the electron density at one of the bromine

‡ The part of nucleophilic coordination in the reactions of organomercury compounds of the aromatic series is evidently less significant. Thus in the triphenylmethylation of arylmercury bromides for both the complex $(C_6H_5)_3CBr.HgBr_2$ and the free $(C_6H_5)CBr$ the transition states probably have an open structure [70].

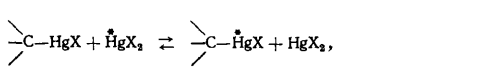
§ "External nucleophilic catalysis" in S_E reactions also receives steady attention from this standpoint. Allowing for this phenomenon we will reconsider some generally accepted positions. For example, the widely accepted view that symmetrical organomercury compounds R_2Hg are more reactive than the organomercury salts RHgX is true only for non-catalytic reactions. Under catalytic conditions (when R_2HgX^- and $RHgX_2^-$ really react) the reactions of fully substituted organomercury compounds and of organomercury salts are accelerated but for the latter compounds the acceleration is considerably greater. As a result under catalytic conditions the organomercury salts react more rapidly than symmetrical organomercury compounds.

atoms is higher than on the bromine atoms in the Br_2 molecule. Hence the greater capability to coordination with mercury atoms:

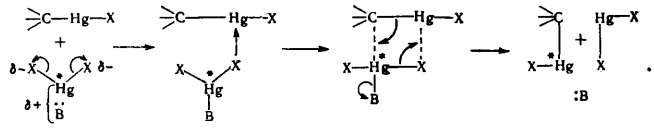


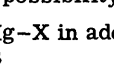
The S_E2 reaction becomes so fast that the competing process — photochemical, free-radical reaction — is suppressed.

In reactions of monoalkyl isotopic exchange:



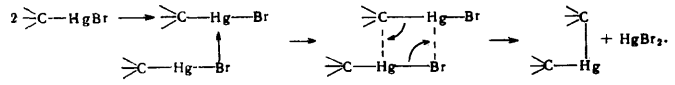
the catalytic action of bases can be explained by the greater tendency of the halogen atoms in $B.\overset{*}{H}gX_2$ complexes to nucleophilic association:



Finally the possibility of the formation of complexes of the type  in addition at a considerable excess of a base must be considered. Here the internal nucleophilic association will be hindered but reaction by an S_E1 mechanism will simultaneously be facilitated.

When the necessity of nucleophilic association is borne in mind it is not surprising that halodemercuration (p. 169) by the S_E2 mechanism takes place easily under the action of the nucleophilic reagent I_3^-,[50-52] etc.

We note, finally, that in the previously considered symmetrisation of organomercury compounds it seems completely possible that the formation of a four-membered cyclic transition state also precedes nucleophilic coordination of a bromine atom with mercury in the pre-kinetic stage:



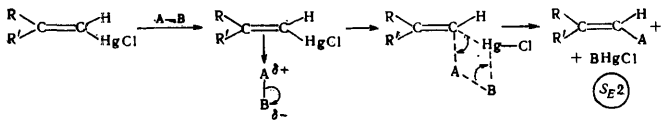
10. THE REACTIVITY OF ORGANOMERCURY COMPOUNDS OF THE ALKENE AND AROMATIC SERIES

As is well known, in general the mechanism of substitutions in saturated, alkene, and aromatic carbon atoms differs significantly.

However, in organomercury compounds it is impossible not to note in the S_E reactions a known similarity due to a general, extremely characteristic replaceable group (HgX, sometimes HgR).

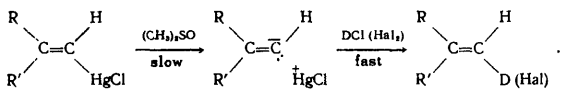
The S_E2 reactions of alkene and aromatic organomercury compounds in low-polar solvents apparently also proceed through a cyclic four-membered transition state[72-77].

For example, the S_E2 reaction of *cis*- and *trans*-β-chlorovinylmercury(II) chlorides and the *cis*- and *trans*-isomers of styrylmercury halides proceed with retention of the configuration[72-74,77]; their mechanism can be represented by the scheme:



(I) R=Cl, R′=H; (II) R=H, R′=Cl,
(III) R=C_6H_5, R′=H; (IV) R=H, R′=C_6H_5

It is interesting that the S_E1 reaction at an alkenic carbon atom also proceeds with retention of the geometrical configuration[73,74]:



The mechanism of protolysis and halodemercuration of aromatic organomercury compounds also has several similar features[75,76] with the mechanism of the same reactions in the aliphatic series.

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PROGRESS IN THE CHEMISTRY OF 2-PYRONES

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I. INTRODUCTION

Many physiologically active compounds contain an α-pyrone ring in their molecule. They include the bufadienolides — heart glycosides of plant and animal origin (bufotalin, cinobufagin, scilliroside, etc.[1-11]), individual representatives of 2-pyrones[12-15] (paracotoin, yangonin, hispidin) which exhibit antibiotic and fungicidal action[16].

In this connection investigations have appeared in the last decade devoted to the development of general methods of synthesis of 2-pyrones, and also the isolation of individual representatives of 2-pyrones from plants and the establishment of their structure.

Derivatives of 2-pyrone were used recently for the synthesis of colchicine[17,18], barrelene[19], and other difficultly accessible compounds.

The present review gives an account of the principal literature on methods of synthesis and the reactivity of 2-pyrones†, indicating the progress in the chemistry of these heterocyclic compounds‡.

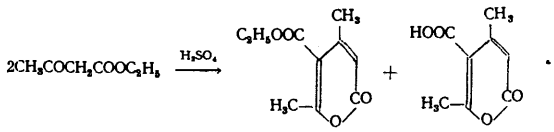
II. METHODS OF SYNTHESIS OF 2-PYRONES

The known methods of synthesis of 2-pyrones can be divided into two types: synthesis from compounds with an open chain of carbon atoms, and from compounds which already contain a six-membered lactone ring.

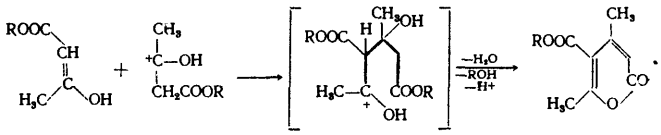
1. CONDENSATION OF β-KETO-ACIDS, β-ALDEHYDO-ACIDS, AND THEIR ESTERS

Condensation in the Presence of Acid Catalysts

One of the longest known methods of synthesis of 2-pyrones is the intermolecular condensation of acetoacetic ester under the action of concentrated sulphuric acid[23] or hydrogen chloride[24-27].

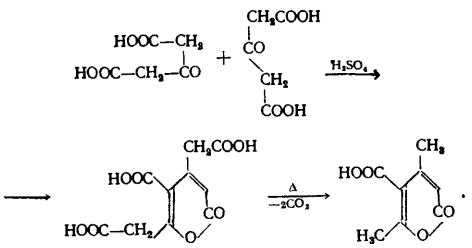


This synthesis of isodehydracetic (2,4-dimethyl-2-oxopyran-5-carboxylic) acid§ and its ester was later studied in detail by Wiley and Smith[28]. According to their suggested mechanism, one molecule of the acetoacetic ester reacts in the enol and the other in the keto- (protonated) form[28]:



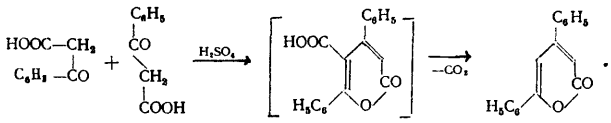
Homologues of isodehydracetic acid and its ester exhibiting bactericidal activity were synthesised in a similar manner[14].

Dibasic β-keto-acids behave analogously in this reaction[34,35]:

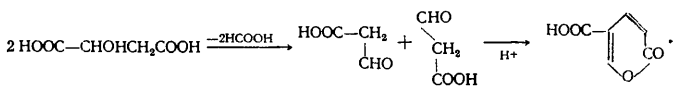


When isodehydracetic acid is heated with concentrated sulphuric acid to 160–170° it is decarboxylated into 4,6-dimethylpyran-2-one[23,36].

Isodehydrobenzoylacetic acid is decarboxylated even at room temperature, therefore the final product of the condensation of benzoylacetic acid is 4,6-diphenylpyran-2-one[37]:



The synthesis of coumalic acid (2-oxopyran-5-carboxylic acid) by heating malic acid with concentrated sulphuric acid and zinc chloride (quantitative yield) apparently proceeds through the stage of formation of a β-aldehydo-acid (the semi-aldehyde of malonic acid), which, like the β-keto-acids, undergoes intermolecular condensation[38,39]:



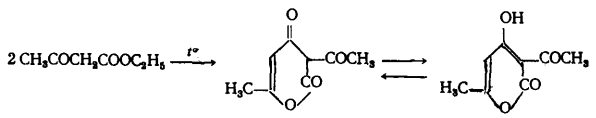
† The literature on the chemistry of the coumarins (benzo[*b*]pyran-2-ones), which exhibit specific properties, is not discussed here.

‡ Cavalieri's review[20] on the chemistry of the pyrones, published in 1947, is out of date. The information about the 2-pyrones given in the monographs edited by Elderfield[21] and by Grignard[22] are also restricted to 1947.

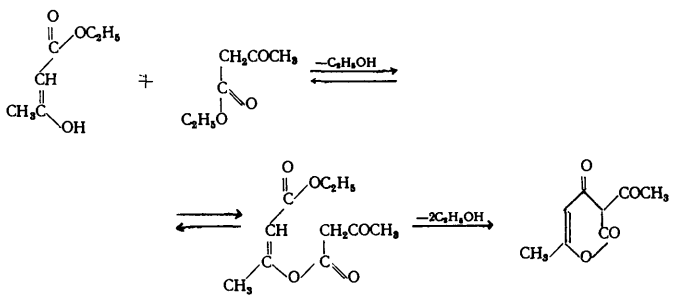
§ Isodehydracetic acid can serve as the starting point for the synthesis of various compounds which are not readily accessible[29,30]; its derivatives are also interesting because of their physiological activity.[31-33]

Condensation in the Presence of Basic Catalysts

Among the thermal decomposition products of acetoacetic ester a substance[40] which received the name dehydracetic acid was observed; later it was ascribed the structure 3-acetyl-6-methylpyran-2,4-dione, which can be found in equilibrium with the tautomeric 3-acetyl-4-hydroxy--6-methylpyran-2-one[41]:

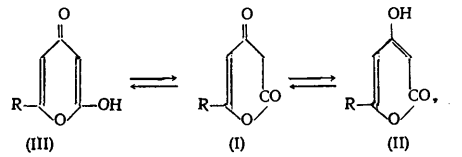


Arndt and coworkers[42-44] suggested that during the pyrolysis a vinyl ester is first formed, which then cyclises into dehydracetic acid (the part of catalyst is played mainly by the walls of the glass reaction vessel):



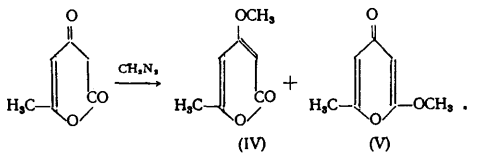
Esters of other β-keto-acids gave in this way alkyl-[45,46], cycloalkyl-[47,48], and aryl-substituted dehydracetic acids[49,50] (some of these compounds exhibit high antibactericidal activity[45,46]).

A notable feature of the compounds of the dehydracetic acid type is their ability when heated with sulphuric acid¶ to lose an acyl group and form 6-substituted pyran--2,4-diones (I)[41-43,52-54]. It is suggested that the latter may exist in two enolic forms — 4-hydroxypyran-2-one (II) and 2-hydroxypyran-4-one (III)[55,56]:

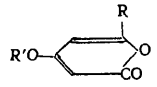


Actually, as infrared and ultraviolet spectra have shown, pyrandiones (pyronones) exist in the form of the 4-hydroxypyran-2-one (II), or the 2-hydroxypyran-4-one (III), or as an equilibrium mixture of (II) and (III), depending upon the substituents, the state of aggregation, and the solvent[57-59].

In the methylation of 6-methylpyran-2,4-dione (and also its analogues) two esters (IV) and (V) were isolated, corresponding to the two possible enol forms[58-65]:



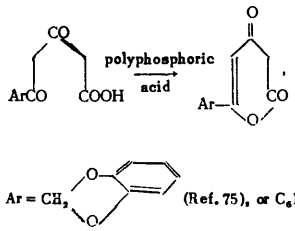
Note that the pyronone nucleus enters into the composition of many physiologically active compounds isolated from plants: yangogin (VI)[66,67], anibine (VII)[68-71], 4-methoxyparacotoin (VIII)[68,70,72], 5,6-dehydrokawain (IX)[72], and hispidin (X)[73,74]:



where R′ = CH_3, R = *p*-$CH_3OC_6H_4CH{=}CH$ (VI); 3-C_5H_4N (VII); 3′,4′-$(CH_2O_2)C_6H_3$ (VIII); $C_6H_5CH{=}CH$ (IX); R′ = H, R = 3′,4′-$(HO)_2C_6H_3CH{=}CH$ (X).

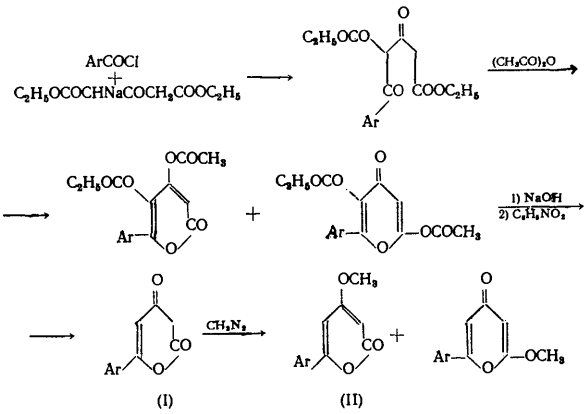
2. INTRAMOLECULAR CYCLISATION OF αδ- AND βδ-DIKETO--ACIDS

Intramolecular dehydration of βδ-diketo-acids leads to the formation of pyran-2,4-diones. Thus the cyclisation of δ-aryl-βδ-diketovaleric acids under the action of polyphosphoric acid (PPA) gives 6-arylpyran-2,4-diones:



where Ar = CH_2 (Ref. 75), or C_6H_5 (Ref. 76).

The cyclisation of the corresponding ester of a βδ-diketo-acid is the principle of a method by which Borsche first synthesised yanganolactone (I) and from it yangonin (II)†[67]:



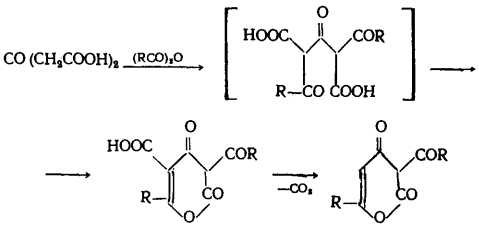
where Ar = *p*-$CH_3OC_6H_4CH{=}CH$.

The cyclisation of βδ-diketo-acids into pyran-2,4-diones sometimes takes place very easily even under conditions

¶ Under the action of hydrohalogen acids dehydracetic acid and its analogues are converted into 2,6-disubstituted 4-pyrones.[41-43,51]

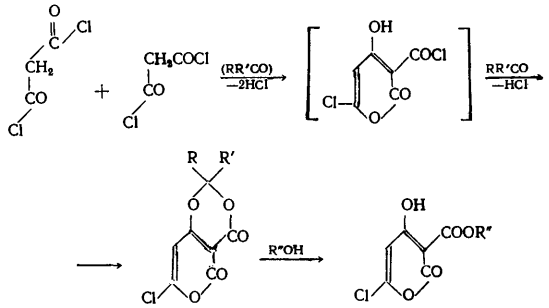
† For the structure of yangonin, see Chmielewska and coworkers.[77,78]

for obtaining the βδ-diketo-acids themselves (for example, under the action of acid anhydrides into acetonedicarboxylic acid[79-81]):

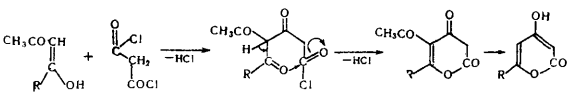


where R = CH_3, C_2H_5, C_3H_7.

Among the conversions of this type must be included the synthesis of 2-pyrones based on malonyl dichlorides‡ and its monoalkyl derivatives. Thus malonyl dichloride itself (in the presence of ketones, which act as weak bases) undergoes the following series of conversions[82]:



In the condensation of malonyl dichloride with acetylacetone, the pyronone isomeric with dehydracetic acid and containing an acetyl group at position 5 is formed[84]. The asymmetric β-diketone gives in these conversions the isomer corresponding to the preferential direction of the enolisation[84]:

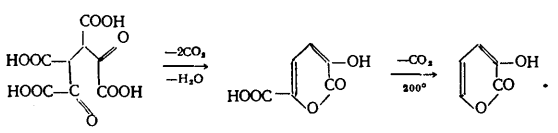


where R = CH_3, C_6H_5.

Esters of β-keto-acids (acetoacetic and benzoylacetic esters) behave similarly in reacting with malonyl dichlorides[85,86].

Hence the condensation of malonyl dichloride and its alkyl derivatives with β-dicarbonyl compounds — apparently proceeding through the stage of formation of acid chlorides corresponding to βδ-diketo-acids (type IV) — can serve as a general method of synthesis of 4-hydroxypyran-2-ones (pyran-2,4-diones).

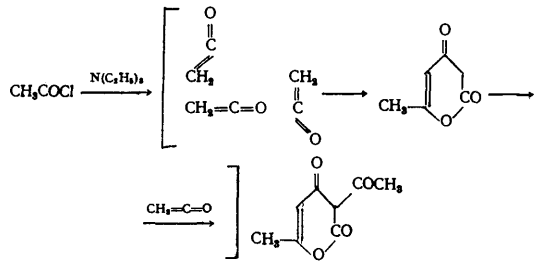
Unlike the βδ-diketo-acids, the αβ-diketo-acids (αα'-dioxalylsuccinic[87,88] and αβ-dioxalylpropionic[89] acids) are cyclised into derivatives of 3-hydroxypyran-2-one, for example:



‡ The condensation of malonyl dichloride in the presence of thiourea with the formation of compounds of the pyronone series has been described, but the precise structure of the products has not been established.[83]

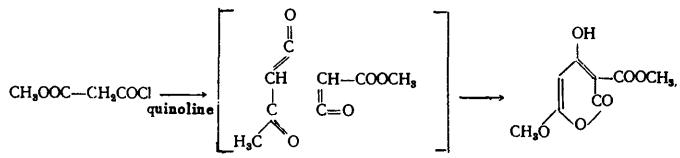
3. KETENS IN THE SYNTHESIS OF 2-PYRONES

2-Pyrones are formed by the action of tertiary amines on the halides of certain acids[90-92]. To explain the nature of the reactions it is assumed that initially ketens are formed, the cyclisation of which also leads to the formation of the corresponding 2-pyrones Thus the formation of dehydracetic acid from acetyl chloride is apparently the result of the trimerisation of keten into pyran-2,4-dione which is acylated further by another molecule of keten in the free 3-position[90]:

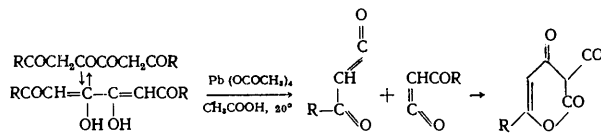


Under the same conditions propionyl chloride forms a homologue of pyran-2,4-dione (trimer of methylketen)[91].

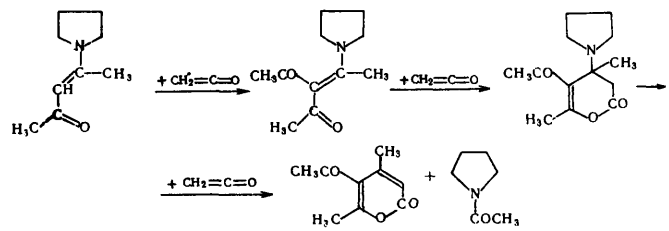
The conversion of methyl chloroformylacetate into a derivative of 2-pyrone evidently proceeds through the intermediate formation of the corresponding keten, which then dimerises[92]:



The action of lead tetra-acetate in acetic acid on 1,3,4,6-tetraketones gives compounds of the dehydracetic acid type; the process can be represented as the dimerisation of an acylketen formed as an intermediate in the splitting of the tetra-ketone[93]:

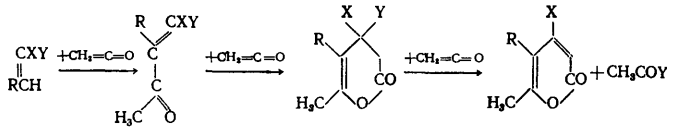


Another possibility of using keten in the synthesis of 2-pyrones consists in its reaction with enamines of carbonyl compounds. Thus, the reaction of the enamine of acetylacetone with keten evidently proceeds as follows[94]:



An ester of isodehydracetic acid is obtained analogously from the enamine of acetoacetic ester, and 1-methyl-3-oxocyclohexano[*c*]pyran from the enamine of cyclohexanone[94].

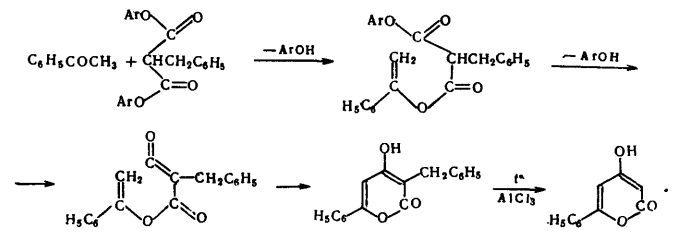
The reaction of keten and its homologues with *NN*- or *ON*-acetals of keten proceeds by the same scheme[95,96]:



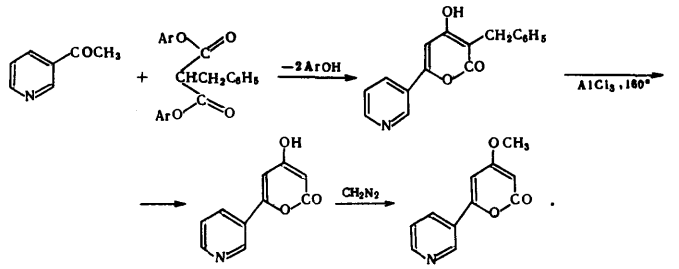
where X = NR'_2, Y = NR'_2, OAlk.

4. THERMAL CONDENSATION OF ESTERS OF SUBSTITUTED MALONIC ACIDS WITH KETONES

It was recently found that the thermal condensation of benzylmalonic esters with ketones which can be enolised can serve as a method for the synthesis of compounds of the 2-pyrone series§, for example[99]:



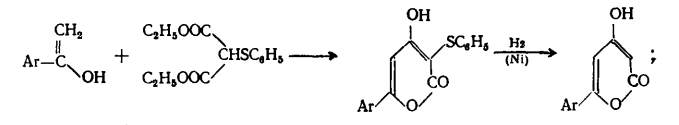
Use of various aliphatic–aromatic[99] and cyclic[100] ketones in this reaction gave (after debenzylation) 4-hydroxypyran-2-ones with a free 3-position[53]. On starting from 3-acetylpyridine, anibine (4-methoxy-6-pyrid-2-yl-pyran-2-one) was obtained by the same method in good yield[101]:



However, 4-methoxyparacotoin (see p. 176) could not be obtained in this way since the ammonium chloride used for debenzylation destroys the piperonyl residue[101].

It was subsequently shown that ethyl esters of malonic acids can be used successfully in this reaction instead of the less readily available diaryloic esters[102,103].

A variant of this method is the use of the diethyl phenylthiomalonate[104,105]:

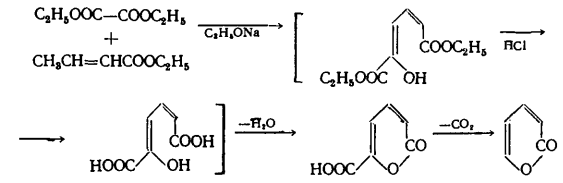


4-hydroxyparacotoin — Ar = 3′,4′-$(CH_2O_2)C_6H_3$ — was obtained in this way.

§ Thermal condensation of malonic esters with phenols is a well-known method of obtaining derivatives of 4-hydroxycoumarin.[97,98]

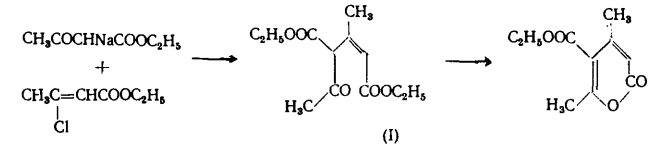
5. CYCLISATION OF αβ-UNSATURATED δ-KETO-ACIDS AND THEIR DERIVATIVES

An important method of synthesis of 2-pyrones is the cyclisation of unsaturated δ-keto-acids and their derivatives, which are often converted into pyrones even under the conditions of their production[106–109]; for example:



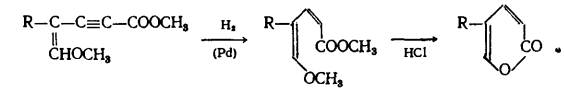
The linear homologues of crotonic ester (RCH_2–CH=$CHCO_2C_2H_5$) give 5-alkyl-2-oxopyran-6-carboxylic acid[110], the thermal decarboxylation of which leads to 5-alkylpyran-2-ones[110,111].

Anschütz and coworkers[112] synthesised ethyl isodehydracetate from the ester of the corresponding unsaturated keto-acid (I):

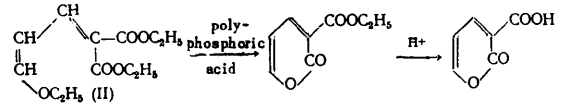


Sometimes αβ-unsaturated keto-acids or their derivatives are so easily cyclised into the corresponding 2-pyrones that their formation in any of these reactions can only be conjectured[113–116].

Attempts to obtain 2-pyrones by cyclisation of αβ-unsaturated δ-aldehydo-acids did not give positive results[110]; however, by using their enol esters for this purpose¶, Panizzi and Nicoletti[117,118] prepared 5-alkyl-substituted 2-pyrones (in poor yield)[117,118]:



In analogous fashion, diethyl 3-ethoxyallylidenemalonic acid (II) is cyclised into ethyl 2-oxopyran-3-carboxylate[119]:

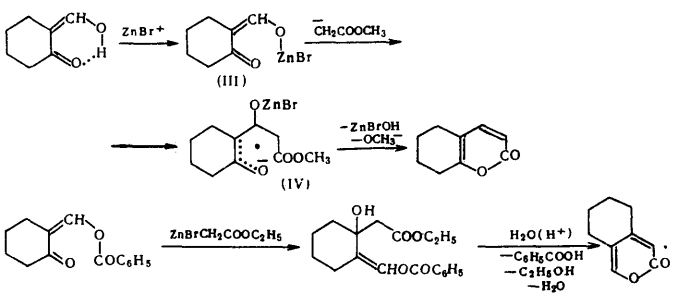


The cyclisation of the ester of the corresponding unsaturated keto-acid can also explain the formation of cyclohexano[*b*]pyran-2-one in the reaction of hydroxymethylenecyclohexanone and methyl bromoacetate (by the Reformatsky reaction).

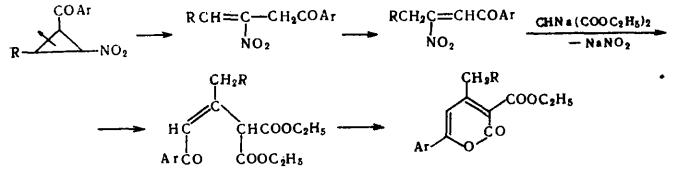
The salt of the enolate (III) gives the condensation product (IV) at the hydroxymethylene group so that only one of the two possible isomers is formed — cyclohexano[*b*]-pyran-2-one[120]. The other isomer, cyclohexano[*c*]pyran-3-one, is obtained on using 2-oxocyclohexylidenemethylbenzoate in this reaction, for which the formation of a salt

¶ Obtained by three-stage synthesis from methoxyacetonitrile.

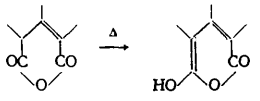
of type (III) is prevented and the reaction proceeds at the carbonyl group[121]:



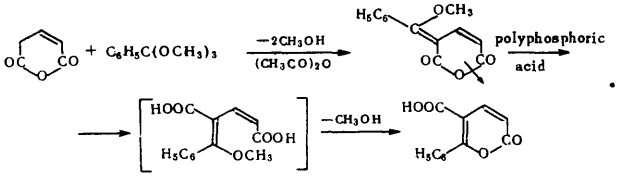
The intermediate formation of esters of $\alpha\beta$-unsaturated δ-keto-acids is also presumed in the production of 2-pyrones by condensation of 1-aroyl-2-nitrocyclopropanes† with bis-(ethoxycarbonyl)methylsodium[122-124]:



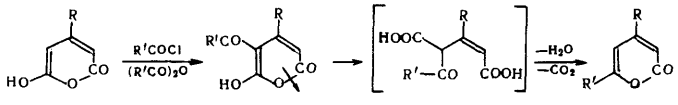
Several methods have recently been proposed for the preparation of 2-pyrones from anhydrides of glutaconic acids, which are characterised by an easy conversion into the isomeric 6-hydroxypyran-2-ones[125,126]:



These methods are also based on the cyclisation of the $\alpha\beta$-unsaturated δ-keto-acids and their derivatives which are formed as intermediates, for example[127]:

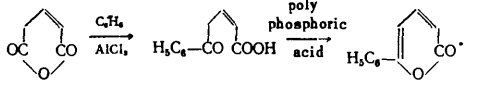


The action of acylating agents on β-methyl- and β-aryl--glutaconic anhydrides gives 5-acyl derivatives, from which it is easy to obtain 6-alkyl-4-methyl-[128-131], 6-alkyl--4-aryl-[132,133], and 4,6-diaryl-pyran-2-ones[134] (with ring opening and recyclisation with participation of the acyl group)[128]:



As a result of such conversions 3,5-diacylated glutaconic anhydrides give 3-acylpyran-2-ones[134].

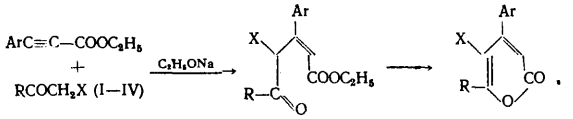
Another path for the use of anhydrides of glutaconic acids consists in their acylation of aromatic compounds; the unsaturated keto-acids thus formed are cyclised further into 6-arylpyran-2-ones, for example[127]:



This method was used with β-substituted glutaconic anhydrides to give a series of 4,6-diarylpyran-2-ones[135-137] and 6-aryl-2-oxopyran-4-carboxylic acids[138].

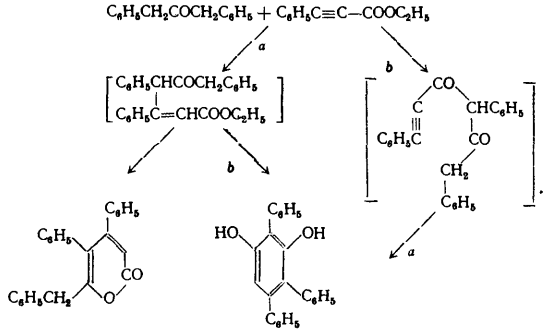
6. CONDENSATION OF $\alpha\beta$-ACETYLENE ACIDS AND KETONES WITH COMPOUNDS CONTAINING AN ACTIVE METHYLENE GROUP

The condensation of esters of propiolic acids with compounds having an active methylene group — benzyl ketones (I)‡[142-144], ω-alkoxy and ω-aryloxyacetophenones (II)[145], esters of β-keto-acids (III)[146-148], β-diketones (IV)[149] — is widely employed for the synthesis of 2-pyrones; their formation is the result of the dehydration of the $\alpha\beta$-unsaturated δ-keto-acids which are formed as intermediates:

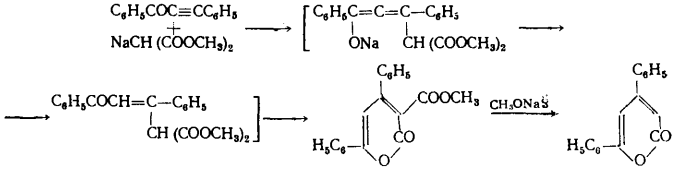


(I) X = C_6H_5; (II) R = Ar, X = OR'; (III) X = $COOC_2H_5$; (IV) X = COR'

Ketones with two active methylene groups form, in addition to the corresponding 2-pyrones, derivatives of resorcinol, the formation of which is explained by the successive occurrence of Michael (*a*) and Claisen (*b*) condensations[150]:



To obtain 2-pyrones use is also made of condensation of ketones of the acetylene series with compounds containing a labile hydrogen atom[151-154], for example[151]:



When the second component in this reaction is methyl α-cyanopropionate, 3-methyl-4,6-diphenylpyran-2-one[156] is obtained.

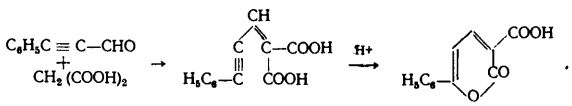
† Under these conditions the corresponding acylnitrocyclopropanes give not only the corresponding 2-pyrones but also appreciable quantities of resorcinol derivatives.[124]

‡ With aliphatic, aliphatic–aromatic, and cyclic ketones the condensation takes place with the formation of derivatives of 4--pyrone.[139-141]

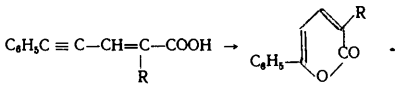
§ It was later shown that the product of the reaction of either 3--carbethoxycarbonyl-6-methyl-4-phenylpyran-2-one[153] or 5-acetyl--6-methyl-4-phenylpyran-2-one[148] with sodium ethoxide is not, however, 6-methyl-4-phenylpyran-2-one.[155]

7. CYCLISATION OF ALKEN-2-YN-4-OIC ACIDS

2-Pyrones can be obtained by the cyclisation of dibasic enynoic acids [109,157] (formed in the condensation of aldehydes of the acetylene series with malonic acid [158-161]) under the action of acidic reagents, for example [109]:

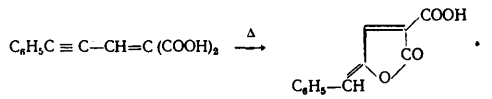


Monobasic enynoic acids are also cyclised in acid media [161-166] or on heating in the presence of mercury sulphate [160], into the corresponding 2-pyrones:

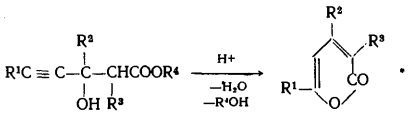


where R = H, or Ar.

However, both types of these acids can also be cyclised (on heating) in another direction — with formation of five-membered unsaturated lactones (derivatives of protoanemonin) [109,162,165], for example:



The cyclisation of enynoic acids forms the basis of a recently proposed method for the production of 4,6- and 3,4,6-substituted 2-pyrones from esters of 3-hydroxy-alkyn-4-oic acids [155]:

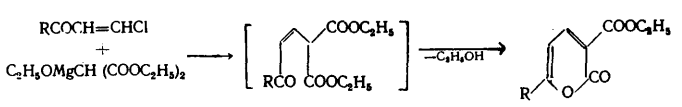


8. 2-CHLOROVINYL KETONES IN THE SYNTHESIS OF 2-PYRONES

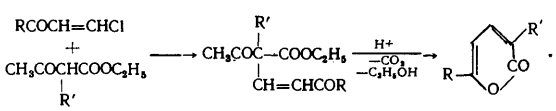
Kochetkov and coworkers used 2-chlorovinyl ketones for making 2-pyrones; these ketones have been widely used in the preparation of other heterocyclic compounds [167].

The reaction of 2-chlorovinyl ketones with substances having a labile α-hydrogen atom leads to the formation of $\beta\gamma$-unsaturated δ-keto-acids, which are readily cyclised into the corresponding 2-pyrones.

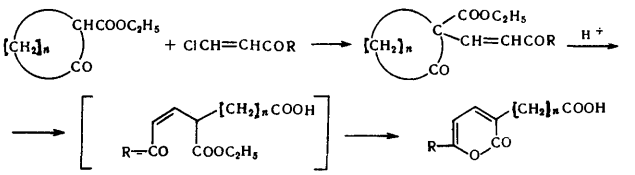
The use in this reaction with 2-chlorovinyl ketones of bis(ethoxycarbonyl)methylmagnesium ethoxide [168,169]:



mono-substituted acetoacetic esters [170,171]:

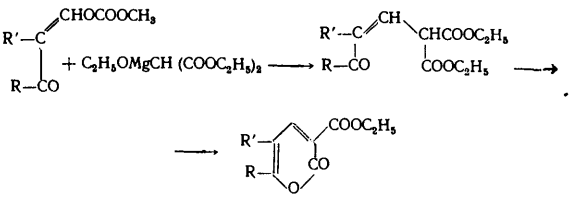


and also esters of cyclic β-keto-acids [170,172]:



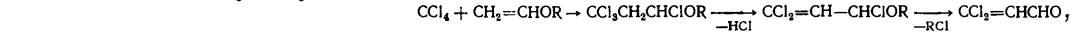
can serve for the preparation of 3,5-disubstituted 2-pyrones.

Analogues of 2-chlorovinyl ketones have been used in this reaction: 2-alkoxyvinyl ketones [173] and *O*-alkoxycarbonyl derivatives of the enol forms of β-dicarbonyl compounds [174]; for example:

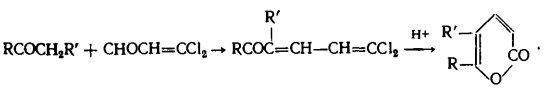


9. $\alpha\beta$-UNSATURATED $\beta\beta$-DICHLOROALDEHYDES AND $\beta\beta$-DICHLOROKETONES IN THE SYNTHESIS OF 2-PYRONES

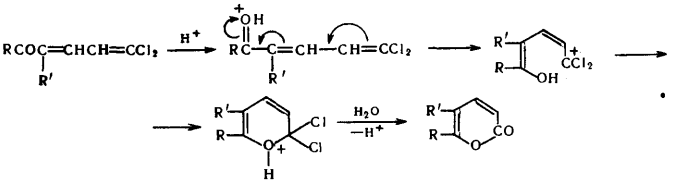
2,2-Dichloroacryladelhyde, which is readily obtainable from the telomer of carbon tetrachloride and vinyl ethers [175,176]:



was the basis of Zakharkin and coworkers' development of a new synthesis of 2-pyrones, the first stage of which is the condensation of dichloroacrolein with alkyl aryl ketones (R = Alk, R′ = Ar) [163,164,177-179] with acetoacetic ester (R = CH_3, R′ = $CO_2C_2H_5$) [177-179], pyruvic acid (R = = CO_2H, R′ = H) [180] under the action of hydrogen chloride [177], metallic sodium [163], or barium hydroxide [164,178]:



The authors put forward the following mechanism for the cyclisation of the 3,3-dichloroallyl diketones which are formed as intermediate [177]:



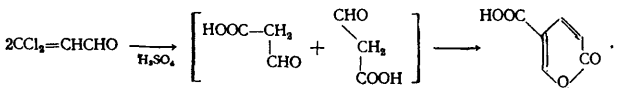
The chloroacetal CCl_2=CH–CHClOR or the telomer $CCl_3CH_2CHClOR$ [181], formed as an intermediate in the preparation of 2,2-dichloroacrylaldehyde, can be used in this reaction instead of the latter.

The use of 2,2-dichloro-1-methylacrylaldehyde allows derivatives of 2-pyrone with a methyl group in position 3 to be obtained [179].

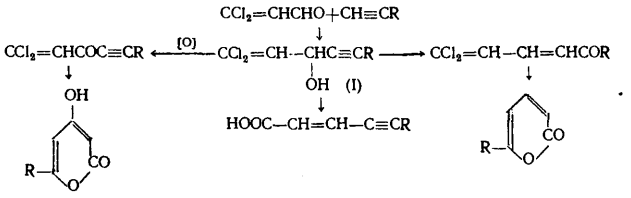
Cyclic β-diketones react with 2,2-dichloroacrylaldehyde [182] or trichloroacrylaldehyde [183,184] to form the corres-

ponding 2-pyrones (without isolation of the intermediate condensation products).

The intermolecular condensation of 2,2-dichloroacrylaldehyde leads to coumalic acid (apparently through the stage of the formation of formylacetic acid)[180]:

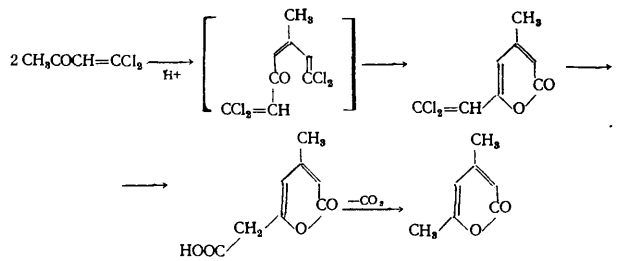


2,2-Dichloroacrylaldehyde was used to make 2-pyrones in another way. On its reaction with the metal derivatives of monosubstituted acetylenes, methanol derivatives (I) were obtained, which were subsequently converted into 2-pyrone derivatives[163,164,178,186]:



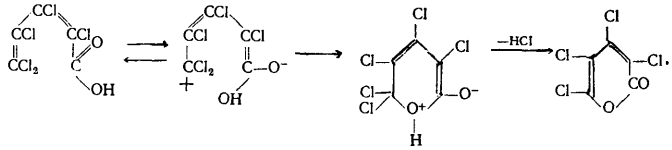
This method was used to prepare paracotoin (6-piperonylpyran-2-one)[164,178] and 3-methyl-6-phenylpyran-2-one[164].

2-Pyrones were also obtained by using 2,2-dichlorovinyl ketones, whose intermolecular condensation takes place by the scheme given above for 2,2-dichloroacrylaldehyde[185]:



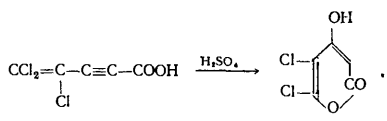
10. CYCLISATION OF POLYCHLORODIENOIC ACIDS

Roedig and Märkl[187] showed that polychlorodienoic acids are cyclised into polychloropyran-2-ones¶ on heating to 180–200°[187,188] or on heating their acid chlorides with concentrated sulphuric acid to 50°:[189]



ω-Bromoperchloropenta-2,4-dienoic acid[187] and perchloropenta-2,4-dienoic acid[190] behave similarly.

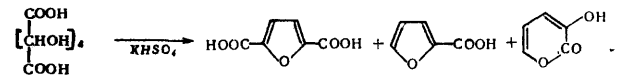
It is interesting to note that trichlorovinylpropiolic acid is converted into 5,6-dichloro-4-hydroxypyran-2-one on standing with concentrated sulphuric acid[191]:



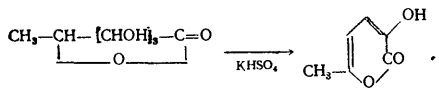
¶ The chlorine atoms in positions 4 and 6 of 2-pyrones are readily replaced by hydrogen on reduction with zinc and acetic acid.[187,190]

11. POLYHYDROXY-COMPOUNDS IN THE SYNTHESIS OF 2-PYRONES

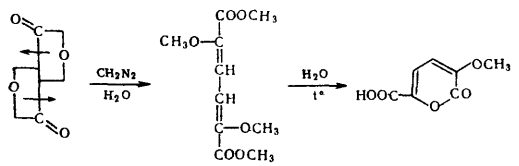
In the dry distillation of mucic acid, in addition to pyromucic (and dehydromucic) acid, an acid isomeric with it is formed, termed isopyromucic acid[192], which, as Chavanne showed[193–198], is 3-hydroxypyran-2-one. A better yield of isopyromucic acid is obtained on heating mucic acid with potassium hydrogen sulphate[198–200] (isopyromucic acid can be separated from pyromucic and dehydromucic acids by making use of their different acidities[201]:



Similarly, 3-hydroxy-6-methylpyran-2-one is formed in the distillation of rhamnolactone[202–204]:



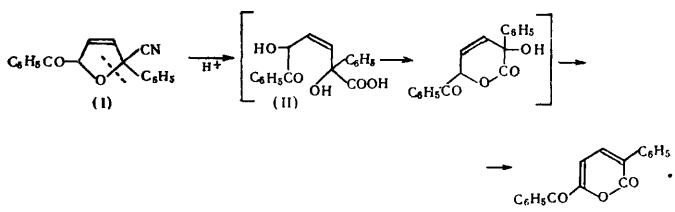
The action of moist diazomethane on the dilactone of mannosaccharic acid gives methyl 2,5-dimethoxymuconate, which is converted on boiling with water into 3-methoxy-2-oxopyran-6-carboxylic acid[105]:



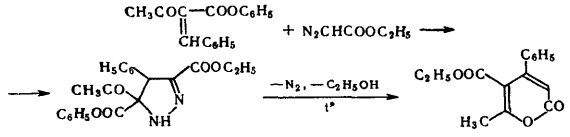
3-Hydroxypyran-2-one and its derivatives are also formed on distilling other polyhydroxy-compounds[198,206].

12. FIVE-MEMBERED HETEROCYCLIC COMPOUNDS IN THE SYNTHESIS OF 2-PYRONES

The conversion of some compounds of the 2,5-dihydrofuran and pyrazoline series into derivatives of 2-pyrones has been described. Thus, in the hydrolysis of substituted 2,5-dihydrofuran (I) the corresponding 2-pyrone is formed — through the intermediate stages of opening of the furan ring with subsequent cyclisation and dehydration of the dihydroxyketo-acid (II) which is formed[207]:

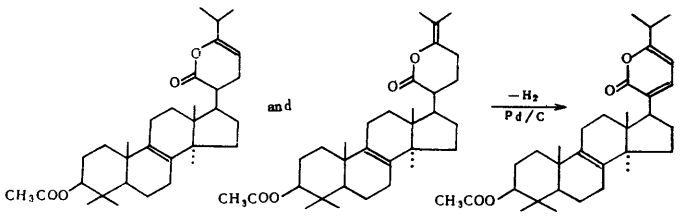


Another example of such a reaction is also well known[208]. The conversion of substituted pyrazolines into the corresponding 2-pyrones has been described[209,210], for example:



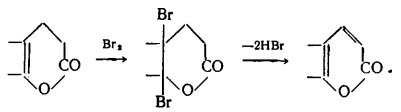
13. δ-LACTONES IN THE SYNTHESIS OF 2-PYRONES

Recently the catalytic dehydrogenation of triterpenoidal δ-enol-lactones into the corresponding 2-pyrones was described[211,212]:



This exhausts the literature on the direct dehydration of δ-lactones.

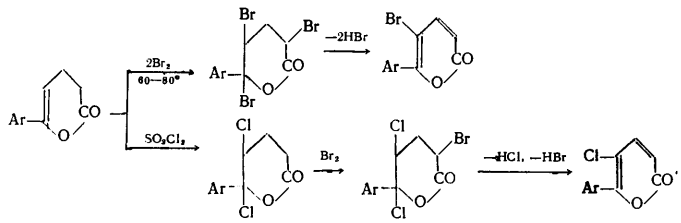
In recent years the indirect dehydration of δ-enol-lactones into 2-pyrones has been developed extensively. Shusherina and coworkers have carried out the conversion of δ-enol-lactones into 2-pyrones by brominating the former and then dehydrobrominating the dibromides which are formed (during their distillation)[213,214]:



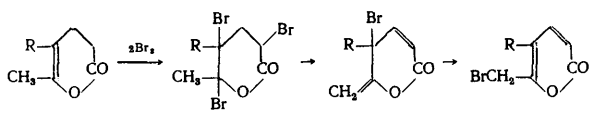
The reaction can serve as a preparative method for obtaining cycloalkano[*b*]- and 5,6-dialkyl- (or 5,6-alkylaryl-) -pyran-2-ones[213,215,216].

The chlorination of δ-enol-lactones (by the action of sulphuryl chloride) with the subsequent dehydrochlorination of the dichlorides was used for the same purpose[217,218].

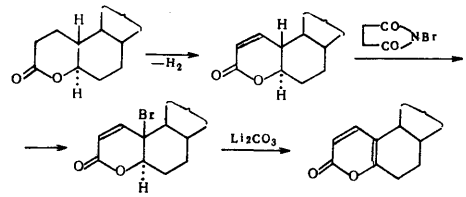
The halogenation of 6-aryl-3,4-dihydropyran-2-ones at the double bond and at the α-methylene group and subsequent dehydrohalogenation is a preparative method for the synthesis of 6-aryl-5-halogenopyran-2-ones[219,220]:



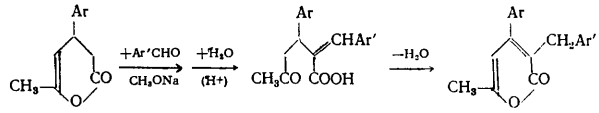
The same series of conversions for 5-alkyl- or 5-aryl- -3,4-dihydro-6-methylpyran-2-ones leads to the production of monohalides of another type — 6-bromomethylpyran- -2-ones, the formation of which is apparently the result of a rearrangement of the intermediate, allyl bromide[221]:



Recently, by the example of steroidal compounds, a method was developed for making 2-pyrones from saturated δ-lactones by partial dehydrogenation in positions 3 and 4 of the lactone ring and subsequent bromination in the allyl position followed by dehydrobromination of the monobromide formed[222]:



What is in principle another method of converting 3,4-dihydropyran-2-ones with an aryl group in position 4† into 2-pyrones has been described — their condensation with aromatic aldehydes and subsequent cyclisation (with isopropenyl acetate) of the α-benzylidene-δ-keto-acids which are formed[223]:



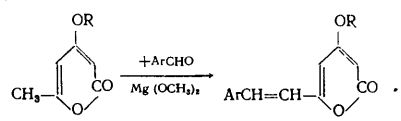
14. PRODUCTION OF 2-PYRONES FROM COMPOUNDS WHICH ALREADY CONTAIN THE PYRONE RING

Reactions of 2-pyrones which take place with retention of the pyrone ring can be used for converting one type of 2-pyrone into another and serve for the production of pyrones of a given structure.

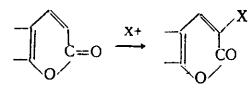
Thus, decarboxylations (see above) are widely used for going from oxopyrancarboxylic acids to 2-pyrones devoid of functional substituents[19,39]. For example, 6-phenylpyran-2-one can be obtained by decarboxylation of all the isomeric 2-oxo-6-phenylpyrancarboxylic acids[115,127,138,160]. The reduction of certain 2-pyrone derivatives is also used for this purpose — 4-chloropyran-2-ones[48], 3-chloromethylpyran-2-ones[224], 5-bromopyran-2-ones[218,219], and 6-bromomethylpyran-2-ones[221].

Homologues of 2-pyranones can be obtained by methylating the pyrone ring with methyl iodide in the presence of potassium hydroxide[225] or with diazomethane[226,227].

The alkyl groups of certain derivatives of 2-pyrone exhibit the ability to undergo condensation with aromatic aldehydes[86,228]. Thus the condensation of esters of 4-hydroxy-6-methylpyran-2-one with corresponding aldehydes gives yangonin[59] and hispidin[229]:



An electrophilic substitution of 2-pyrones recently completed allows derivatives of 2-pyrones with a functional substituent in the 3-position to be obtained[230-235]:



where X = NO_2, SO_3H, SO_2Cl, CH_2Cl.

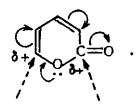
† When there is not an aryl group in position 4, then unsaturated lactones with one double bond in the ring and the other in the exocyclic position are formed.

III. CHEMICAL PROPERTIES OF 2-PYRONES

2-Pyrones exhibit an unusual combination of properties, of which the best known is their ability as unsaturated lactones to react with various nucleophilic reagents. The ability of 2-pyrones to enter into diene synthesis has been much less studied. The electrophilic substitutions of 2-pyrones which characterise these heterocyclic systems as aromatic have been investigated only recently.

1. REACTION OF 2-PYRONES WITH NUCLEOPHILIC REAGENTS

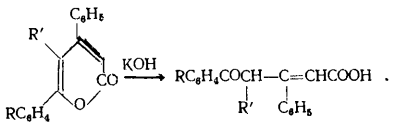
Nucleophilic reagents whose action on 2-pyrones is accompanied by ring opening attack the pyrone ring in position 2 or 6‡, which agrees with the representation of the electron density distribution in the α-pyrone ring:



In which of these directions any particular reagent will react is apparently determined mainly by the thermodynamic stability of the addition products which are formed[236].

Hydrolysis

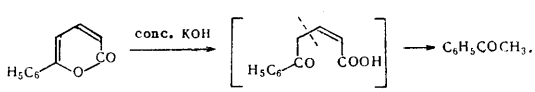
Under the action of aqueous or alcoholic solutions of alkalis the pyrone ring is broken and unsaturated δ-keto-acids are formed[68,72,73,120,135,137,144,145,242,243§]; for example[145]:



The production of unsaturated δ-keto-acids as hydrolysis products can be considered as the result of the addition of water to the α-pyrone ring at the 1,2- or 1,6-bonds.

In individual instances the unsaturated keto-acids are very easily cyclised (on acidifying the salts) into the original 2-pyrones[225].

Hydrolysis of 2-pyrones with concentrated alkali is frequently accompanied by subsequent hydrolytic splitting¶ of unsaturated keto-acids[20,26,39,68,142,243,247]; for example[246]:

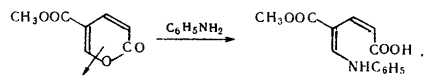


Examples are known of great stability in the α-pyrone ring under hydrolysis conditions. Thus, 3,5-di-t-butylpyran-2-one could be hydrolysed only by prolonged heating with alkali at 150° (in glycerol solution)[243].

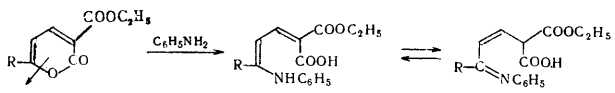
Reaction with Ammonia and Amines

Unlike hydrolysis, the addition of ammonia or amines to 2-pyrones can lead to different reaction products, depending on whether the 1,2- or the 1,6-bond of the α-pyrone ring is broken.

Pechmann and Welsh[248] showed that in the reaction of methyl coumalate with aniline δ-anilino-γ-methoxycarbonylsorbic acid is formed, that is, primary amines are attached at the 1,6-bond of the α-pyrone ring:

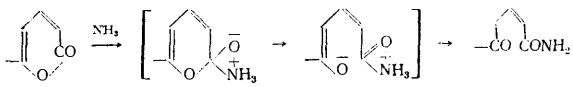


Such a presentation of the way 2-pyrones react with ammonia and primary amines is also confirmed by the results of Kochetkov and Kudryashov[249], who obtained 2-ethoxycarbonyl-5-phenyliminoalkadienecarboxylic acids by the reaction of 6-alkyl-3-ethoxycarbonylpyran-2-ones with aniline:



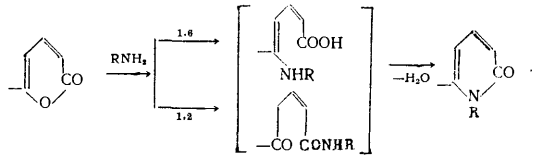
where R = CH_3, C_3H_7, C_5H_{11}.

A second possible direction of the reaction of 2-pyrones with ammonia and amines has also been discussed in the literature[187,251,252]; it is accompanied by breaking of the 1,2-bond of the α-pyrone ring and leads to the production of amides of unsaturated δ-keto-acids; it is suggested that the reaction starts here with attack of the carbonyl group of the 2-pyrone[251]:



However, such a course of the reaction has not been confirmed.

Usually the action of ammonia and primary amines on 2-pyrones gives 2-pyridones, the formation of which can be considered, in the light of the above data, to be the result of the dehydration of addition products which are formed initially:



The conversion of 2-pyrones into pyridones under the action of ammonia occurs both in the cold[35,123,124,151,187,247,248,253-255], and on heating[112,113,144,145,256,257]; instead of ammonia, ammonium acetate is sometimes used[107,110,189,258-260,266].

The production of *N*-substituted pyridones[187,248,250,256,259,261-265,267] by the action of primary amines on 2-pyrones (in the cold or on heating) is often used for confirming the structure of 2-pyrones.

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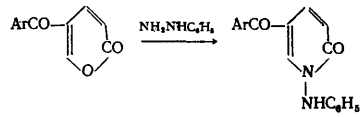
‡ Saturated and unsaturated γ and δ lactones also react with nucleophilic reagents along these two directions[237,238] but usually under milder conditions than for pyrones.[239-241]

§ The action of alkali metal alkoxides on 2-pyrones leads to the formation of esters of unsaturated δ-keto-acids.[126,151,246]

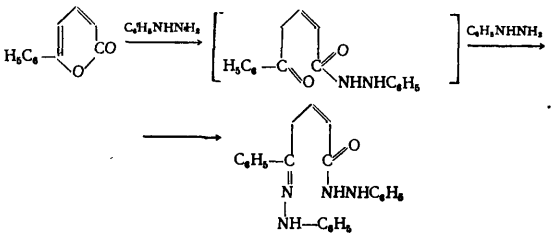
¶ Therefore the hydrolysis of 2-pyrones is not used for their identification in distinction from the hydrolysis of δ-enol-lactones, (3,4-dihydropyran-2-ones).[244,245]

The reaction of 2-pyrones with phenylhydrazine leads either to *N*-substituted pyridones or to the amides of δ-keto--acids.

Thus, 5-aroylpyran-2-ones readily react with phenylhydrazine to give the corresponding *N*-aminopyridones[256]:



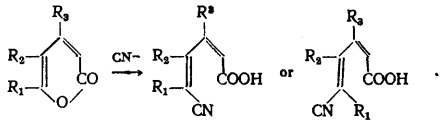
where Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, whereas 6-phenylpyran-2-one forms the phenylhydrazide of the corresponding unsaturated δ-acid (isolated as the phenylhydrazone)[225]:



The reaction of 2-pyrones with hydrazine, hydroxylamine, and semicarbazide leads to the formation of *N*-substituted pyridones[144,145,257,268]†.

Reaction with Sodium Cyanide

Recently Vogel[270] carried out a new reaction of opening the α-pyrone ring at the 1,6-bond under the action of the cyanide ion, which leads to the formation of mononitriles of unsaturated acids of the muconic acid type:



The stereochemical directionality of this astonishingly easy reaction (it ends after 5–10 min in the cold) can be controlled by choice of solvent.

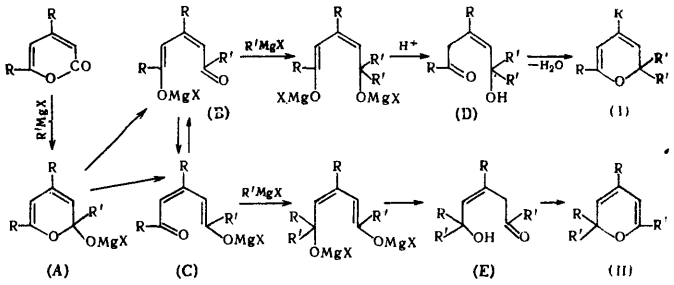
Reaction with Grignard Reagents

The reaction of pyrones with organomagnesium compounds is quite complicated. Gompper and Christmann[271], who first studied this reaction, ascribed to the compounds obtained the structure of pyrans (I):



(I)

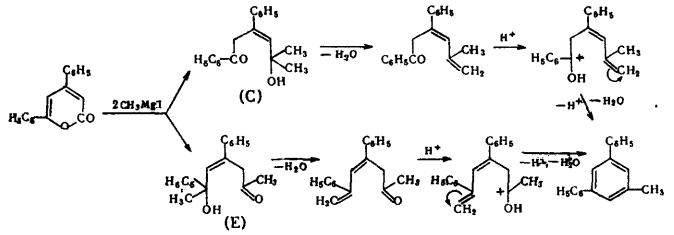
It was shown later[272] that pyrans of structure (II) can also be formed which is explained[273] by the existence of an equilibrium between the two forms of enolates, (B) and (C), which are formed from the initial addition product (A):



(A) (B) (C) (D) (E) (I) (II)

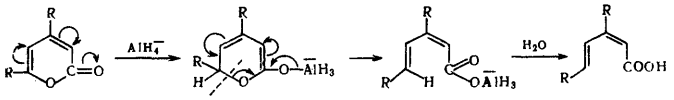
When the pyrone is taken in excess at R or R′ = Ar then aromatic hydrocarbons are formed in 60–80% yield[95,274].

Apparently, the keto-alcohols (D) and (E) are dehydrated initially into doubly-unsaturated ketones, which are cyclised subsequently by a Prins type of intramolecular reaction[275], for example:



Reduction by Hydro-Complexes of Metals

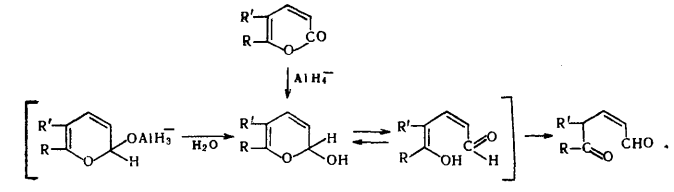
Hydro-complexes of metals react with 2-pyrones to reduce these to unsaturated acids[276–278] (or under more severe conditions — to unsaturated alcohols[211,212,277,278]), the formation of which is explained, apparently, by the addition of an aluminium hydride anion at the carbonyl group of the 2-pyrone and the hydride ion at position 6 and by subsequent opening of the ring at the 1,6-bond:



Hence the final result of this conversion is the hydrogenolysis of the 1,6-bond of the α-pyrone ring‡.

† Wiley and coworkers[269] showed that the action of hydrazine on ethyl isodehydracetate takes place anomalously with the formation of 3-methylpyrazol-5-one.

‡ However, in other instances during the reduction of 2-pyrones by lithium tetrahydroaluminate hydrogenolysis of the 1,2-bond of the α-pyrone ring takes place with formation of unsaturated δ-keto--aldehydes[279] or of the products of their further reduction — unsaturated 1,5-diols[280,281]; for example[279]:



The ease of reduction depends both on the structure of the initial 2-pyrone and on the activity of the metal hydro-complex used. Thus, coumalic acids are reduced at even 0–10° by such mild agents as sodium or lithium tetrahydroborate [277,278].

Sodium or lithium tetrahydroborate very readily reduces 4-methoxy-6-methylpyran-2-one, being converted into the corresponding unsaturated acid; the action of lithium tetrahydroaluminate forms a further reduction product — an unsaturated alcohol [278]. 4,6-Dimethylpyran-2-one is reduced to an unsaturated acid only by lithium tetrahydroaluminate [277,278].

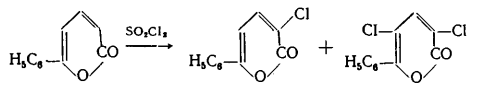
2. ELECTROPHILIC SUBSTITUTIONS IN THE 2-PYRONE SERIES

In accordance with the polarisation of the bonds of the α-pyrone ring it must be expected that the attack of electrophilic reagents will be directed to the third or fifth carbon atom of the ring.

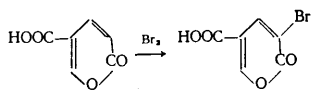
(a) Halogenation

Chlorination. The action of chlorine on coumalic [254] and isodehydracetic [26] acids gave the corresponding monochloro-substituted acids. The position of the chlorine atom was shown by the conversion of one of them (chlorocoumalic acid) into the known 3-chloropyridine [254].

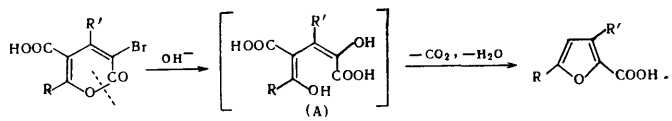
It was recently shown that the chlorination of 2-pyrones takes place very readily under the action of sulphuryl chloride [282]. Thus, under its action 6-phenylpyran-2-one is converted even in the cold into a mixture of mono- and di-chloro-derivatives:



Bromination. Bromination is one of the most studied substitutions of 2-pyrones. Under the action of bromine replacement of one or two (depending on the reaction conditions and the structure of the initial pyrone) hydrogens of the α-pyrone ring takes place. Thus, during the bromination of isodehydracetic [23,26,31,33] and coumalic [28,248,256,253] acids and their esters the corresponding monobromo-derivatives were obtained, for example [248]:

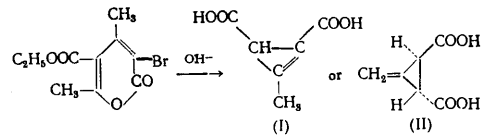


To prove the position of the bromine atom, Feist [26,283,284] used the alkaline hydrolysis of these bromo-substituted 2-pyrones; the hydroxy-acids which are formed as intermediates in the opening of the pyrone ring are cyclised into the corresponding α-furancarboxylic acids, the formation of which is possible only when the bromine atom in the initial bromopyrones is in position 3:



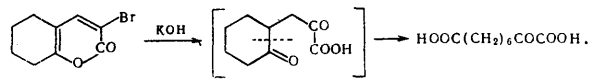
Conversion into α-furancarboxylic acids was used to establish the structure of the bromination products of other 2-pyrones [37,209,247,285–287]. However, examples have been described of the anomalous behaviour of bromopyrones under the action of alkalis.

Thus, in the alkaline hydrolysis of the ethyl ester of brominated isodehydracetic acid [112] a substance was isolated [26,284] which is best known in the literature as Feist's acid, for which two structures were proposed later — 2-methylcyclopropene-1,3-dicarboxylic acid (I) [27] and *trans*-3-methylenecyclopropane-1,2-dicarboxylic acid (II) [288]:



Bottini and Roberts [292] supported structure (II) on the basis of a study of NMR spectra.

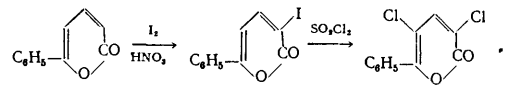
Another example, which illustrates the anomalous behaviour of bromopyrones in reacting with alkali is the formation of α-ketoazelaic acid from 3-bromo-5,6,7,8-tetrahydrochromen-2-one [289]:



In the bromination of 2-pyrones in which positions 3 and 5 are free, the bromine enters the 3 position in the cold [37,128,129,185,191] and on heating into the positions 3 and 5 with the formation of dibromopyran-2-ones [290,291].

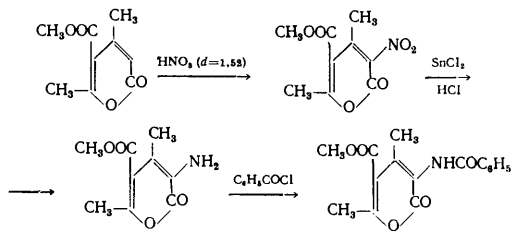
Hardly anything has been published on the reactivity of bromopyran-2-ones. Pechmann [254] described an unsuccessful attempt to replace the bromine atom in bromopyrones by the action of various nucleophilic reagents, showing at the same time the exceptional inertness in these reactions of the bromine connected to the α-pyrone ring.

Iodination. It was recently shown, by the example of 6-phenylpyran-2-one, that under conditions of oxidative iodination (118°, in the presence of concentrated nitric acid) iodine enters the pyrone ring to form 3-iodo-6-phenylpyran-2-one, the structure of which was confirmed by conversion into the well-known 3,5-dichloro-compound§ [282]:



(b) Nitration

The nitration of 2-pyrones was first carried out by Angeli [293], by the example of methyl isodehydracetate; the structure of the reaction product was shown much later [294] by the reduction of the nitro-group and the subsequent benzoylation of the amine formed:

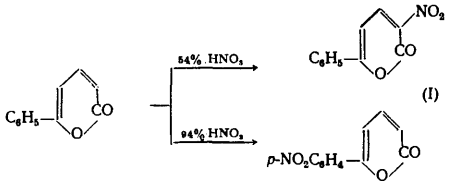


§ The iodination of 3-hydroxypyrone by iodine in the presence of yellow mercury oxide has been described [198], but the structure of the monoiodopyran-2-one thus obtained has not been established.

In other studies it was assumed, by analogy with brominations, that the nitro-group enters the 3-position [33,231,295].

Ciamician and Silber [225] obtained 3-nitro-6-phenylpyran-2-one on nitrating 6-phenylpyran-2-one with 70% nitric acid¶; its structure was recently shown by Zakharkin and Sorokina [246] who converted it into α-amino-δ-phenylvaleric acid. On the basis of this the authors [246] drew the general conclusion that the nitration of 6-phenylpyran-2-one by nitric acid takes place only in the pyrone ring.

However, Shusherina and coworkers [296] showed that by varying the nitric acid concentration 6-phenylpyran-2-one can be selectively nitrated. Thus, when 94% nitric acid is used the nitro-group only enters the benzene ring but with 54% nitric acid only in the pyrone ring:



(I)

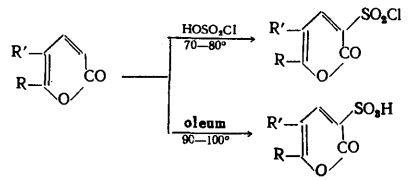
(II)

This feature of the behaviour of 6-phenylpyran-2-one is evidently explained by the greater stability of the oxonium complex in more concentrated acid, which should lead to a decrease in the reactivity of the α-pyrone ring as regards the electrophilic substitutions [296].

In the nitration of 6-phenylpyran-2-one [290] and isomeric methylphenylpyran-2-ones [231] with nitrating mixture, the nitro-group enters only the benzene ring.

(c) Sulphochlorination and Sulphonation

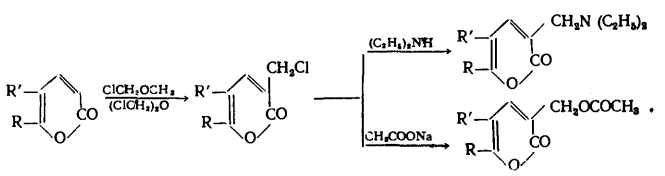
Shusherina and coworkers first effected the sulphochlorination [232] (yield 30–50%) and sulphonation [233] (yield ~ 50%) of 5,6-disubstituted pyran-2-ones:



where R = R′ = CH_3; or R = CH_3, R′ = C_3H_7, C_4H_9.

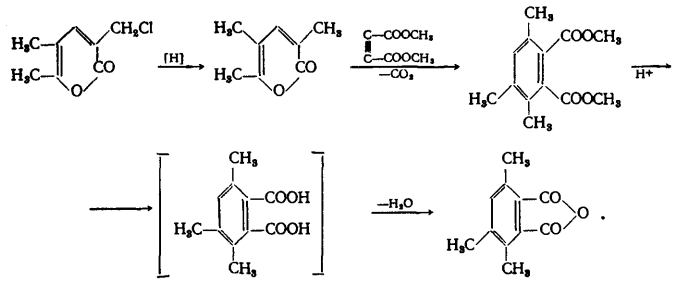
(d) Chloromethylation

2-Pyrones are chloromethylated in position 3 under the action of a mixture of mono- and bis-chloromethyl esters or of formalin saturated with hydrogen chloride. The chloromethylpyran-2-ones obtained (yield 35–41%) readily undergo exchange reactions [234,235]:



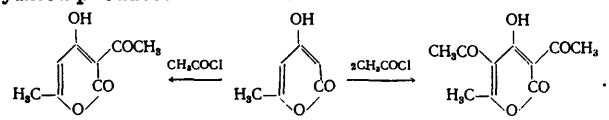
¶ The authors of the present article have shown that in addition to 3-nitro-6-phenylpyran-2-one under these condicitions 6-*p*-nitro-phenylpyran-2-one is also formed (ratio 8 : 1). [290]

The position of the chloromethyl group was shown by converting 3-chloromethyl-5,6-dimethylpyran-2-one into a homologue of phthalic anhydride with a known position of the substituent [224]:



(e) Acylation

As yet the Friedel-Crafts reaction has been accomplished only for hydroxypyran-2-ones. Thus in the acylation of 4-hydroxy-6-methylpyran-2-one acyl chlorides of carboxylic acids form a mixture of the mono- and di-acylated products [54,85,291,298]:



4-Hydroxy-6-methylpyran-2-one is an example of a compound which has been formylated [297] by a mixture of carbon monoxide and hydrogen chloride in the presence of trifluoroacetic acid, but the structure of the products of the reaction has not been shown.

From the reactions considered in this section it has long been known that for pyrones halogenation and nitration are not typical of an electrophilic substitution, since they can proceed either by an ionic or by a radical mechanism. Possibly this is why 2-pyrones were not considered to be aromatic systems until recently.

The suggestion that 2-pyrones were of aromatic character was made recently by Mayer [300], who drew this conclusion on the basis that 2-pyrone is an isoelectronic analogue of tropone:



Such typical electrophilic substitutions as sulphuration, sulphochlorination [232], chloromethylation [235], and nitration with nitrating mixture [231] which have been performed for pyrones confirm Mayer's hypothesis and allow this class of heterocyclic compounds to be placed among non-benzenoid aromatic systems.

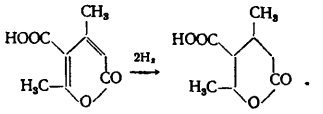
The conclusion about the aromatic nature of 2-pyrones and also about the similarity of 2-pyrones with tropones was confirmed recently [301,302] by Sheinker and coworkers from a study of the intensity of the absorption bands of the carbonyl group in the infrared spectra of 2-pyrones.

3. REACTION OF ADDITION AT THE DOUBLE BONDS OF THE α-PYRONE RING

A characteristic of the 2-pyrones is reactions which involve compounds with a system of conjugated double bonds — catalytic hydrogenation and diene synthesis.

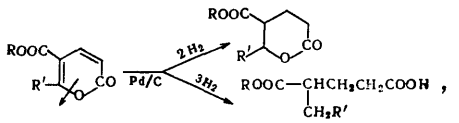
(a) Catalytic Hydrogenation

2-Pyrones easily add on hydrogen at the double bonds to form lactones — tetrahydropyran-2-ones, for example[303]:



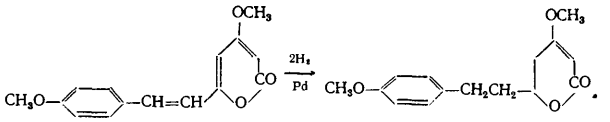
Hydrogenation catalysts which have been used for 2-pyrones are: palladium on carbon[129,303], barium sulphate[170,304], and also palladium black[305].

In addition to the addition of hydrogen at the multiple bonds of the α-pyrone ring, under catalytic hydrogenation conditions hydrogenolysis of the 1,6-bond is observed, leading to the formation of acids[226,303] (sometimes as the main product of the reaction):



where R = R′ = H and CH_3.

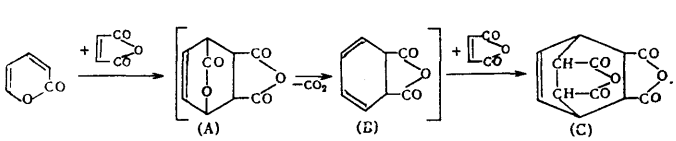
Selective hydrogenation (in the 5,6 position) of the α-pyrone ring has been achieved under certain conditions[305-307]. Thus yangonin gave 5,6-dihydro-4-methoxy--6-(*p*-methoxyphenethyl)pyran-2-one, the narcotic action of which is connected specifically with the absence of a double bond in the 5,6 position of the α-pyrone ring[307]:



Catalytic hydrogenation was used to prove the structure of certain natural compounds containing an α-pyrone ring — scillaren A[8], cinobufagine[6], bufotalinin, and marinobufagin[308].

(b) Diene Synthesis

A distinctive property of 2-pyrones is their ability to undergo the diene synthesis. On studying the reaction of 2-pyrone and methyl coumalate with maleic anhydride, Diels and Alder[309] showed that a mono-addition product (A)† is formed at 110°, which is decarboxylated at 130–140° into the 1,2-dihydrophthalic anhydride (B); the latter reacts with another molecule of maleic anhydride, forming a bridging addition product (C):



(A) (B) (C)

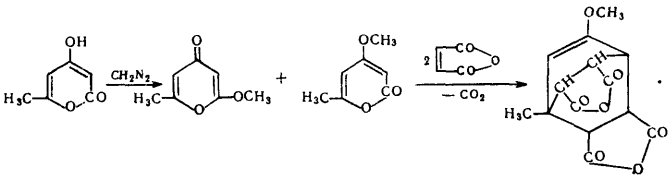
It was subsequently found that apart from the temperature the essential factor determining the course of the reaction is the structure of the 2-pyrone. Thus 5-alkylpyran-2-ones[110,117] like the pyrones studied by Diels and Alder[309] form mono-addition products with maleic anhydride at 110°, whereas 5,6-dialkylpyran-2-ones under these conditions give only the di-addition products[213].

Di-addition products are also formed by 5,6-dialkyl--substituted 2-pyrones containing bromine[230] or acetoxy or chloromethyl groups[224,234,235] in position 3. With polychloropyrones[311] the course of the diene synthesis depends on the number of chlorine atoms in the α-pyrone ring. Thus 3,4,5,6-tetrachloropyran-2-one forms only a di-addition product, whereas the 3,5,6-trichloro- and 3,5-dichloro-pyran-2-ones give mono- and di-addition products.

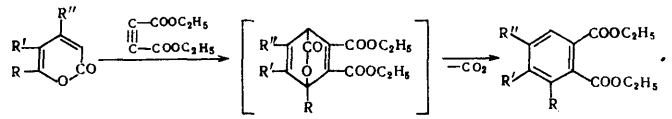
The presence in the 3 position of the α-pyrone ring of such electronegative substituents as a nitro-, sulpho-, or carboxyl group[123,231] completely deactivates the diene system of the 2-pyrones, making it incapable of undergoing the diene synthesis.

The formation of crystalline di-addition products with maleic anhydride‡, which usually occurs with excellent yields and is accompanied by the characteristic liberation of carbon dioxide, can serve as an excellent method for the identification of 2-pyrones[120,138,208,213,215].

Bu′ Lock and Smith[59] used this reaction to demonstrate the structure of the product of the methylation of 4-hydroxy--6-methylpyran-2-one, which was a mixture of the methoxy--derivatives of the corresponding γ- and α-pyrones, of which only the latter reacted with maleic anhydride:

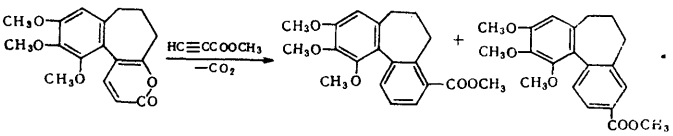


The use of diethyl butyndioate[59,312,313] as a dienophile in reaction with 2-pyrones has been described; the reaction is accompanied by the evolution of carbon dioxide and leads to the formation of the corresponding esters of phthalic acid:



This reaction was used to obtain difficultly accessible derivatives of phthalic acids[18,314].

Methyl propiolate reacts with substituted 2-pyrones to give both possible reaction products — the corresponding esters of the *ortho*- and *meta*-substituted benzoic acids[18]:

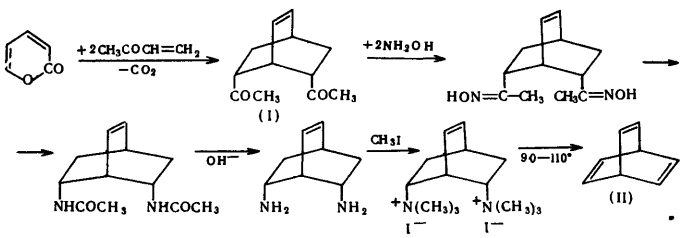


The ability of 2-pyrones to undergo the Diels–Alder reaction has recently been used in organic synthesis. Thus one of the isomeric di-addition products of 2-pyrone with

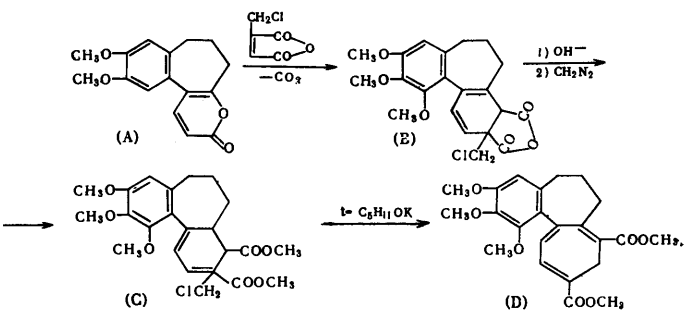
† The endo-configuration of the addition product (A) was recently confirmed by measurement of its dipole moment.[310]

‡ The formation of di-addition products was also observed in the reaction of 2-pyrones with acrylonitrile[246] and *N*-phenylmaleimide.[95]

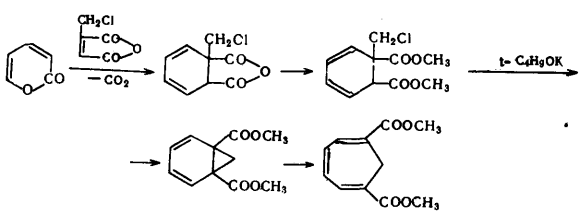
methyl vinyl ketone (I) was used in the synthesis of barrelene, bicyclo[2,2,2]octa-2,5,7-triene[19]:



The diene synthesis of the tricyclic 2-pyrone (A) with chloromethylmaleic anhydride was used to synthesise the ester (D) having the colchicine carbon skeleton[17,18]:

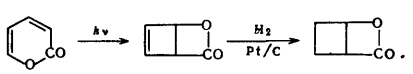


The analogous reaction of coumalin with 2-chloromethylmaleic anhydride can be used for the preparative production of cycloheptatriene-1,3-dicarboxylic acid[315]:



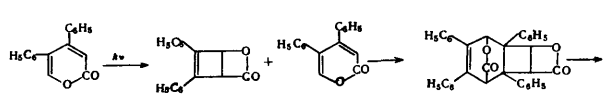
4. PHOTOISOMERISATION OF 2-PYRONES

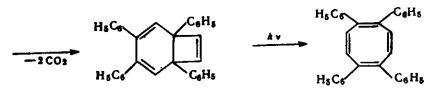
It was recently shown[316] that under the action of ultraviolet light 2-pyrone isomerises into a β-lactone condensed with a cyclobutene ring (the yield is almost quantitative); the structure of the β-lactone was confirmed by the formation of an addition product with isobenzofuran and also by hydrogenation into the corresponding saturated β-lactone:



This interesting reaction was recommended by the authors for the preparation of compounds of the cyclobutane series.

The example of 4,5-diphenylpyran-2-one showed[317] that the β-lactone formed initially undergoes a diene synthesis with the original pyrone under the conditions of the reaction to form an addition product, which on further irradiation is converted into the tetraphenylcyclo-octatetraene:





The published work on the reactivity of 2-pyrones shows that the long-held view of the 2-pyrones as doubly-unsaturated six-membered lactones does not exhaust all the peculiar properties of this heterocyclic system. Now it is also recognised to possess aromatic properties, which should be ascribed to the 2-pyrones on the basis of their recently discovered ability to undergo typical electrophilic substitutions.

The variety of chemical properties of the α-pyrone ring which is apparent in their capability for photoisomerisation, to diene synthesis, and also to react with various nucleophilic reagents (for example, the Grignard reagent, potassium cyanide), allows 2-pyrones to be widely used in organic synthesis for obtaining difficultly accessible compounds of the cyclobutane, cyclo-octatetraene, cycloheptatriene, and pyran series, derivatives of muconic acid, etc.

These results acquire greater importance in that 2-pyrones themselves, thanks to the many methods of preparation developed in recent years, have become available.

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HYDROGEN BONDS AND π-COMPLEXES IN RADICAL LIQUID-PHASE REACTIONS

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1. INTRODUCTION

The investigation of the influence of the solvent on the kinetics of radical liquid-phase reactions is of considerable importance for the theory of reactivity. The interaction of a reacting species with solvent molecules alters the electronic structure and reactivity of the species. From a knowledge of this interaction it is possible to obtain important information about the factors influencing the reactivity of the reacting species. There is, moreover, another practical aspect of this problem, associated with the choice of solvent and the improvement of technological processes.

The strongest specific interactions exerting a significant influence on the kinetics and sometimes also the mechanism of liquid-phase radical reactions are those revealed in hydrogen bonds and π-complexes. The aim of the present review is to examine the part played by these interactions in kinetics and to reveal their nature and mechanism, that is to analyse the structural-kinetic aspect of specific interactions.

2. HYDROGEN BONDS IN RADICAL REACTIONS

The problem of the part played by hydrogen bonds in the kinetics of chemical reactions was first raised by Emanuel'.[1] A later review[2] examined a large amount of material on the influence of hydrogen bonding on the kinetics and mechanism of many reactions (chiefly ionic). Numerous studies carried out since that time have confirmed conclusively that the manifestation of hydrogen bonding is one of the fundamental characteristics of liquid-phase kinetics. Much of the mechanism by which hydrogen bonding affects the rate of radical reactions is not yet clear, however.

It is first of all important to know whether a reaction takes place through equilibria involving the association of the reacting species by hydrogen bonding and if so, which of the constants of the multi-stage equilibrium are important. It is possible that the reaction involves not only free non-associated molecules, but also solvates, so that hydrogen bonding is also manifested in the activated complex. The coordination number of the solvated complex is then always of considerable importance.

Physical methods of study (X-ray diffraction, electron diffraction, infrared spectroscopy, nuclear magnetic resonance, etc.) make it possible to obtain extensive thermodynamic information on the structure of the solvates, their coordination numbers, and the equilibrium constants for a large number of classes of substances. This material has been collected in a number of reviews and monographs[3-5]. Different methods often give contradictory information on the structure of solvates, but even if the structure of the associated forms is fairly well known, it is difficult to estimate the part which they play in kinetics: for this, kinetic analysis of the influence of association on the reaction rates is necessary.

In radical reactions, each of the participants in the reaction — the molecule and the radical — may be associated. Let us consider first the influence of association of the molecules on the rate of their reactions.

In the study of the decomposition of hydroperoxides, which are the primary products of the oxidation of most organic and many inorganic compounds, it has been established that at sufficiently high concentrations of the hydroperoxide, its decomposition obeys the kinetic equation for a first-order reaction and apparently proceeds according to the scheme

$$2\mathrm{ROOH} \rightarrow \mathrm{R\dot{O}_2} + \mathrm{H_2O} + \mathrm{R\dot{O}}. \qquad (1)$$

This has been observed in the decomposition of ethyl linoleate[6], cyclohexyl[7], tetralin[8], n-decyl[9], t-butyl[10], and cumene hydroperoxides.

It was assumed that the hydroperoxide molecules are associated by hydrogen bonding to form dimers[6,11], and that their decomposition to give radicals is thereby facilitated considerably. The association of hydroperoxides was in fact confirmed by physical methods[7,12], but kinetic proof of the preferential participation of the associated hydroperoxide in decomposition according to scheme (1) was given only recently in papers by Denisov[10,13]. An analogous effect of increase in the rate of decomposition is brought about by intramolecular hydrogen bonding in acyl hydroperoxides[1].

The decomposition of hydroperoxides is also facilitated by the presence of other substances capable of undergoing association with the hydroperoxide molecules by hydrogen bonding, for example alcohols[14], organic acids[15], etc. This phenomenon was studied in detail[16] for the decomposition of n-decyl hydroperoxide in the presence of hexanoic acid. It is assumed that the decomposition scheme is

$$\mathrm{ROOH} + n\,\mathrm{R'COOH} \overset{K}{\rightleftarrows} (\text{associate}) \overset{k}{\rightarrow} \dot{\mathrm{R}}\mathrm{O} + \dot{\mathrm{O}}\mathrm{H} + n\,\mathrm{R'COOH}. \qquad (2)$$

It was shown that the coordination number n of the associate, that is the number of molecules of acid in the complex with the hydroperoxide, is equal to 2; the equilibrium constants K and the constants k for the decomposition of the complex to form radicals were also determined. The activation energy for the decomposition of the hydroperoxide in the associate (16.1 kcal mole^{-1}) was found to be much less than that for the decomposition of the hydroperoxide in the absence of the acid (23.8 kcal mole^{-1}). All these facts indicate that hydrogen bonding occurs in the elementary stages of the decomposition of the hydroperoxides to form radicals. A detailed analysis of the mechanism of decomposition involving hydrogen bonding, from the viewpoint of the heats and activation barriers of the elementary reactions, was given by Berezin[17].

In radical substitutions (in particular, in the most extensively studied reactions involving hydrogen atom abstraction), the presence of associates of molecules reacting with one another or with solvent molecules by hydrogen bonding means that both free molecules and their associates may take part in the reaction, at different rates. Kinetic proof for this differentiated participation is given in a number of papers.

Thus Berezin's work[17,18] on the oxidative decarboxylation of decanoic acid according to the scheme

$$\mathrm{RCOOH} + \mathrm{r}\dot{\mathrm{O}}_2 \rightarrow \mathrm{r\,OOH} + \mathrm{RC}\!\!<\!\!\begin{matrix}\dot{\mathrm{O}}\\ \mathrm{O}\end{matrix}$$
$$\mathrm{RC}\!\!<\!\!\begin{matrix}\dot{\mathrm{O}}\\ \mathrm{O}\end{matrix} \rightarrow \dot{\mathrm{R}} + \mathrm{CO}_2 \qquad (3)$$

where rO_2 represents the peroxide radical of the hydrocarbon rH in which the decarboxylation takes place, established convincingly that only monomeric non-associated acid molecules take part in the reaction (3), the acid dimers formed by hydrogen bonding being quite inactive.

Study of the reaction of diethyl phosphite with the tri-t-butylphenoxyl radical[19] showed that the effective rate constant for the reaction in benzene increases considerably with decrease in the concentration of phosphite. Kinetic analysis of this dependence showed that the free tri-t-butyl phenoxyl reacts much more rapidly with the monomeric form of the phosphite than with the associated form, the coordination number of which is two. Thus here also the monomeric molecules are found to be much more active than the molecules associated to form dimers.

Hydrogen bonding is revealed most clearly in the kinetics of radical reactions with strongly associated molecules such as alcohols and phenols. The analysis of these reactions has now yielded a sufficiently clear picture of the mechanism and nature of the kinetic influence of hydrogen bonding.

Berezin[17,20] showed that the rate constant for the reaction between the methyl radical and t-butyl alcohol with a tritiated hydroxyl group according to the scheme

$$\dot{\mathrm{C}}\mathrm{H}_3 + (\mathrm{CH}_3)_3\,\mathrm{COT} \xrightarrow{k_{OT}} \mathrm{CH}_3\mathrm{T} + (\mathrm{CH}_3)_3\,\dot{\mathrm{C}}\mathrm{O} \qquad (4)$$

depends to a marked extent on the concentration of the alcohol in n-heptane; with increase in the alcohol concentration, the reactivity of free methyl with respect to the hydroxyl group decreases sharply. This agrees with the idea that only monomeric t-butyl alcohol molecules react with methyl radicals. Detailed kinetic analysis showed that the associates apparently have a cyclic structure; it was also possible to determine the thermodynamic characteristics of the association equilibrium. This work confirmed earlier qualitative observations that associated hydroxyl groups in alcohols are unreactive[21].

The association of phenols has an analogous influence on the reactivity of their hydroxyl hydrogen atoms with respect to methyl radicals[17]; the same is true of the reactions of phenols and amines with peroxide radicals[22]. The hydroxyl hydrogen of alcohols is also comparatively inert with respect to hydrogen atom abstraction[23].

The influence of the medium on the kinetics of the reactions of nitrophenols with the stable tri-t-butylphenoxyl radical, involving the removal of hydroxyl hydrogen, has also been studied[24,25]. For o-nitrophenol, the rate constants for this reaction and the activation energies are quite independent of the nature of the solvent in which the reaction takes place (benzene, hexane, acetone, or methanol), but for m-nitrophenol the medium has a marked influence not only on the rate constants but also on the activation energies (Table 1). A linear relationship between the logarithms of the pre-exponential terms and the values of the activation energy, that is a compensation effect, is observed. The compensation effect is apparently due to the influence of the medium; this influence is localised and is determined by the interaction between the reaction centre and the solvent. The dielectric properties of the solvent have no significant influence on the reaction rate constants even for such dipolar species as the phenoxyl radical and phenol; this follows from the data for o-nitrophenol. This also indicates, in particular, that the reacting radical is not solvated (apparently because of steric hindrance). Comparison of the results for o- and m-nitrophenols indicates that the hydroxyl hydrogens of o-nitrophenol do not form hydrogen bonds with the solvent because of the steric hindrance created by the nitro-group and also because of the strong intramolecular hydrogen bond. When the acetone or alcohol is diluted with inert solvents (heptane), the

TABLE 1. Pre-exponential factors k_0 and activation energies E for the reaction of m-nitrophenol with tri-t-butylphenoxyl.

Solvent	k_0, cm^3 s^{-1}	E, kcal mole^{-1}
Benzene	$8\cdot10^{-16}$	10.2
Acetone	$5\cdot10^{-14}$	14.7
Methanol	$6\cdot10^{-13}$	17.3

m-nitrophenol associates are broken down, yielding the more reactive molecules of the monomeric phenol and a corresponding increase in the effective rate constant[25].

The reaction of a radical with a molecule capable of undergoing solvation can be represented in the following general form:

$$\begin{aligned} \dot{R} + XOH_0 &\xrightarrow{k_0} RH + X\dot{O} \\ \dot{R} + XOH_S &\xrightarrow{k_S} RH + X\dot{O} \\ XOH_0 + nS &\overset{K}{\rightleftarrows} XOH_S \\ X\dot{O} + \dot{R} &\xrightarrow{k_1} XOR \end{aligned} \qquad (5)$$

where $\dot{R}$ represents any reacting radical (for example $\dot{C}H_3$, tri-t-butylphenoxyl, or the peroxide radical), and XOH_0 and XOH_S the reacting molecules of a phenol or alcohol with a free hydroxyl group or with a hydroxyl group solvated by n solvent molecules respectively. This scheme assumes that the radical reacts with the free and solvated molecules with the respective constants k_0 and k_S, and also that solvation equilibrium is established.

With the condition that $k_1 \gg k_0$ and $k_1 \gg k_S$, analysis of scheme (5) leads to the following expression for the rate of disappearance of $\dot{R}$ radicals:

$$-\frac{d[\dot{R}]}{dt} = 2\,\frac{k_0 + k_S K[S]^n}{1 + K[S]^n}[\dot{R}][XOH]_\Sigma,$$

where $[XOH]_\Sigma$ denotes the total concentration of reacting molecules of the phenol or alcohol, and [S] the concentration of solvating molecules. The effective rate constant is given by the expression

$$k_{eff} = \frac{k_0 + k_S K[S]^n}{1 + K[S]^n} \qquad (I)$$

and depends on the concentration [S].

Relationship (I) was analysed for the example of the reaction of tri-t-butylphenoxyl with m-nitrophenol in mixtures of acetone or alcohol as solvating solvents with an inert solvent (heptane)[25]. At low degrees of dilution with heptane, that is with the condition that $K[S]^n \gg 1$, Eqn. (I) can be transformed into

$$k_{eff} = \frac{k_0}{K[S]^n} + k_S\,. \qquad (II)$$

By differentiating expression (II) with respect to the concentration [S] and taking logarithms, we obtain the equation

$$\log\left|\frac{dk_{eff}}{d[S]}\right| = \log\frac{k_0 n}{K} - (n+1)\log[S]. \qquad (III)$$

From Eqns. (II) and (III) and the experimental dependence of the effective constant k_{eff} on the concentration of solvating solvent [S] it is possible to determine the coordination number n and to calculate the values of k_0/K and k_S.

Fig. 1 shows the dependence of k_{eff} on the concentration of acetone in its mixtures with heptane, and also the logarithmic form of this dependence, which satisfies Eqn. (III). The slope of the straight line *2* gives $n = 1$ and the intercept on the axis of ordinates gives the value $k_0/K = 1.7 \times 10^{-3}$ s^{-1}. From Eqn. (II) we then obtain $k_S = 1 \times 10^{-26}$ cm^3 s^{-1} (at 22°). The coordination number n is also equal to unity for the reaction in methanol.

If the reacting molecule undergoes association not with the molecules of the medium but with other similar molecules, the reaction can again be described by a scheme

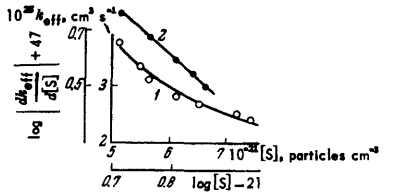


Fig. 1. Dependence of k_{eff} on the concentration of acetone in its mixtures with heptane (curve 1) and its logarithmic transform (straight line 2) [according to Eqn. (III)] for the reaction of m-nitrophenol with tri-t-butylphenoxyl.[25]

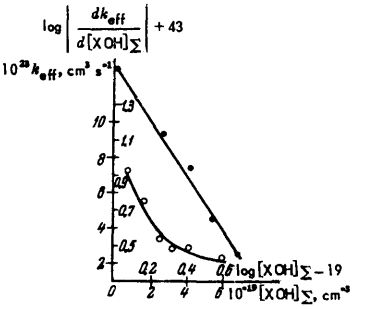


Fig. 2. Dependence of k_{eff} on the concentration of m-nitrophenol and its logarithmic transform [according to Eqn. (IV)] for the reaction of m-nitrophenol with tri-t-butylphenoxyl.[25]

similar to scheme (5), and the corresponding analysis gives the equation

$$\log\left|\frac{dk_{eff}}{d[XOH]_\Sigma}\right| = A + \left(\frac{1}{n} - 2\right)\log[XOH]_\Sigma, \qquad (IV)$$

where A is a constant. From Eqn. (IV) and the data given in Fig. 2 it follows that for the self-association of m-nitrophenol the coordination number $n = 2$.[25]

It should be noted that the coordination number of the solvate complex in the thermodynamic sense denotes the number of solvating molecules present in the complex. The coordination number n appearing in the kinetic equations has its kinetic significance, which does not coincide with the thermodynamic concept. It denotes the number of reactive molecules or groups liberated or held in the elementary equilibrium step of hydrogen bond rupture and formation. Thus in the kinetic equations we cannot use the coordination numbers obtained by physical methods, although in certain particular cases the absolute values of the kinetic and thermodynamic coordination numbers may coincide.

As already noted, in the associates of m-nitrophenol with solvent molecules the value of the kinetic coordination number is unity. This means that only the association of one solvent molecule is significant for kinetics; further association and further growth of the solvate sheath are not significant. In the self-association of m-nitrophenol[25] or diethyl phosphite[19], however, the kinetic coordination number is equal to two, that is two reaction centres take part in the act of complex formation. Thus the reactions of the radicals with the solvated molecules are not elementary reactions, but involve at least three elementary acts: the reaction of the radical with the free non-solvated molecule,

the reaction with the solvate, and the solvation equilibrium. The effective rate constants naturally depend on the concentration of reacting molecules (self-association) or the degree of dilution by an inert solvent (solvation by the solvent). These dependences indicate the existence of specific interactions between the reagents and the molecules of the medium, and they can often be used to investigate the detailed mechanism.

An extremely significant fact in kinetics is that a reaction centre solvated by hydrogen bonding is completely unreactive [18-20] or, strictly speaking, so little reactive that $k_S \ll k_0$. [25]

One reason for this is probably steric hindrance of the reactive group in the solvate. This suggestion alone is obviously insufficient, however, since the distance corresponding to the hydrogen bridge is fairly large and often cannot prevent a reaction by steric hindrance alone. It is clear, for example, that in the reactions of a hydrogen atom, the lack of reactivity of associated hydroxyl groups [23] cannot be attributed entirely to steric effects. Another reason is apparently that the formation of a hydrogen bond in a complex of the type A–H... B leads to partial transfer of charge from the donor B to the acceptor molecule [26] and an increase in the polarity of the reacting bond A–H. This is indicated by the increased intensity of the stretching vibrations of the A–H bond in the infrared spectra, and also by the dipole moments of the complexes and the dielectric properties of substances containing hydrogen bonds [26-29]. The important contribution made by the structure with charge transfer $A^-...H...B^+$ in the complex with hydrogen bonding is also indicated by the linear relationship between the displacement of the stretching and bending vibration frequencies in the hydrogen bridge [30] and by experimental results on NMR chemical shifts on the ^{14}N nucleus of pyridine taking part in hydrogen bonding with methanol [31].

Moreover, there are grounds for assuming that the hydrogen atom in the complex A–H... B is positively charged relative to an ordinary hydrogen atom which is not forming a hydrogen bond, the electron density deficit amounting to 15–20%. This is indicated by electron diffraction data [32], and also by calculation of the NMR chemical shifts (in the one-electron approximation) [33]. It is true that the question of the degree of ionicity of the hydrogen atom is still open [26], but from the kinetic viewpoint the polarisation of the A–H bond in the complex A–H... B is apparently the chief factor leading to the sharp decrease in its reactivity.

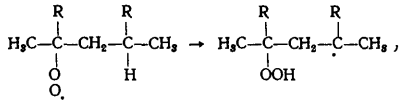
Hydrogen bonding manifests itself not only in the kinetics of radical substitutions, but also in additions across a double bond. Thus *ortho*-substituted *N*-phenylmethacrylamides, whose molecules do not show intermolecular interaction by hydrogen bonding, are polymerised much more rapidly than their *meta*- and *para*-isomers, whose molecules are associated [34].

Until now we have been considering the association of reacting molecules. Let us now consider the influence of association of the radicals on the rate and mechanism of radical reactions. Here two cases are possible: firstly, when the radical forms hydrogen bonds with molecules with which it does not react, and secondly when hydrogen bonding by the radical precedes formation of the activated complex, that is the radical is solvated by the molecule or group with which it reacts. As shown below, the kinetic manifestations of these two possibilities are fundamentally different.

In a study of the decomposition of acetyl peroxide [35] it was shown that the acetyl radicals are more stable in acetic and propionic acids than in aliphatic solvents. This stabilisation of the decomposition of the acetyl radical was attributed to hydrogen bonding between the radical and the acid molecule.

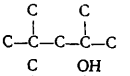
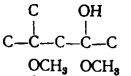
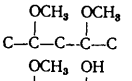
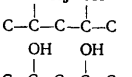
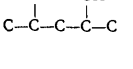
The retarding influence of added water on the oxidation of cyclohexanone was noted by Denisov [36], who showed that this phenomenon is due chiefly to a decrease in the rate constant for chain propagation. This decreased activity of the peroxide radical was assumed to be due to solvation of the radical by water molecules. The proposed kinetic scheme, according to which solvated and non-solvated radicals take part in chain propagation with different rate constants, shows satisfactory agreement with the experimental data. In this paper Denisov formulated clearly for the first time the idea that the participation of radicals in hydrogen bond formation was quite reasonable, and the kinetic consequences of this participation. Subsequent work fully confirmed these ideas.

Thus Rust and Youngman [37], in a study of the oxidation of 2,4-dimethylpentane and 2,4-dimethoxypentane, showed that in these hydrocarbons oxidation proceeds very intensively through intramolecular attack by the peroxide radical on the tertiary C–H bond in the γ-position:

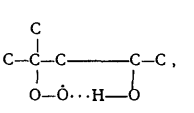


(6)

where R represents a methyl or methoxy group. If one or both of the methyl or methoxy groups are replaced by hydroxyl groups, however, the ability of the hydrocarbons to undergo intramolecular attack by the peroxide radical disappears almost completely. This is effectively illustrated by the scheme given below.

Hydrocarbon	Proportion of products of intramolecular attack, %
	95
	<1
	60–70
	<7.5
	<1

The absence of intramolecular attack (6) in the hydroxyl-containing molecules indicates unambiguously that the peroxide radical forms an intramolecular hydrogen bond of the following type:



which decreases its reactivity with respect to the intramolecular attack at the C–H bond and even leads to a change in the direction of the attack, that is to a change in the oxidation mechanism.

In a number of studies of hydrocarbon oxidation, measurements have been made of the ratios of the constants $k_1/\sqrt{k_2}$ for the reactions of peroxide radicals:

$$\dot{RO}_2 + RH \xrightarrow{k_1} RO_2H + \dot{R}$$
$$\dot{RO}_2 + \dot{RO}_2 \xrightarrow{k_2} O_2 + \text{stable products},$$

in various solvents. It was found that the ratio $k_1/\sqrt{k_2}$ is much smaller in solvents capable of solvating the $\dot{RO}_2$ radical by hydrogen bonding than in inert solvents. This was observed by Howard and Ingold[38] for the oxidation of tetralin and cumene in acetic acid and t-butyl alcohol, by Hendry and Russell[39] for the oxidation of alkenes and arylalkyl hydrocarbons in ethanol and acetic acid, and by Denisov[40] for the oxidation of isopropyl alcohol in methanol and water. These phenomena can be explained on the basis of the theory that the reactivity of the $\dot{RO}_2$ radical is decreased by solvation.

The most convincing proof of solvation of the peroxide radical was obtained by Zaikov and coworkers[41], who measured not only the ratios $k_1/\sqrt{k_2}$, but also the actual constants k_1 and k_2. They showed that solvation of the peroxide radical (in the oxidation of methyl ethyl ketone in aqueous solutions) decreases its reactivity with respect to both chain propagation and disproportionation; the solvate is much less reactive than the free radical, and the coordination number of the solvate is equal to unity. The kinetic data were also used to determine the heat of solvation of the $\dot{RO}_2$ radical.

Walling and coworkers[42-44] studied the competition between two reactions of the t-butoxyl radical — decomposition (7) and substitution (8):

$$(CH_3)_3CO\cdot \xrightarrow{k_{decomp}} (CH_3)_2CO + CH_3\cdot \qquad (7)$$
$$(CH_3)_3CO\cdot + RH \xrightarrow{k_{subst}} (CH_3)_3COH + R\cdot \qquad (8)$$

and the influence of solvents on the quantitative ratio of the products of these reactions. They showed that in a solvating solvent such as acetic acid the difference in the activation energies of reactions (7) and (8), equal to (E_{decomp} - E_{subst}), decreases sharply relative to the value in the gaseous phase or in inert solvents. This effect was attributed to the influence of solvents (and in particular hydrogen bonds) on the activated complex of reaction (7), which is thereby facilitated, with a corresponding decrease in the activation energy E_{decomp}, and hence in the difference (E_{decomp} - E_{subst}). In view of the observation of Levy and Szwarc[35] that the acetyl radical is stabilised by hydrogen bonding, however, it is difficult to suppose that in the present instance hydrogen bonding will facilitate the decomposition of the $(CH_3)_3C\dot{O}$ radical. It appears more probable that hydrogen bonding by the t-butoxyl radical hinders the substitution (8), leading to an increase in E_{subst} and hence to the experimentally observed decrease in the difference (E_{decomp} - E_{subst}). This interpretation explains the results obtained[42-44] and does not contradict the ideas developed by Denisov[36] and confirmed in other work.

The kinetic effects associated with the localised specific interactions between the reacting molecules and radicals and the solvent molecules must apparently be related for the most part not to the activated complex but to the original state, since the lifetime of the activated complex is much less than the characteristic durations of these specific interactions. This remark naturally does not refer to such universal interactions as the dipole–dipole interaction, manifested in the dependence of reaction rates on the dielectric constant of the medium. An example is provided by the detailed work of Zaikov, Maizus, and Emanuel'[45,46] on the influence of the medium on the rate of oxidation of hydrocarbons, alcohols, and ketones, and also by the work of Hendry and Russell[39] on the oxidation of alkenes and arylalkyl hydrocarbons in various solvents.

Thus in all cases when the radical forms hydrogen bonds with those molecules with which it does not react, the result is a decrease in its reactivity in the main reaction; the reaction consists of the ensemble of elementary acts of chain propagation (with the participation of the non-solvated radical and the solvate) and equilibria of radical solvation.

If, however, the radical forms a hydrogen bond with the molecule with which it subsequently reacts, this association facilitates the reaction considerably. Effects of this type were observed by Szwarc and Smid[47] for the decomposition of propionyl and benzoyl peroxides in acetic and trifluoroacetic acids. The ethyl radicals obtained by decomposition of the $C_2H_5C(=O)O\cdot$ radical react with the acids at the C–H or C–F bond. In the decomposition of benzoyl peroxide, the $PhC(=O)O\cdot$ radicals are relatively stable with respect to decomposition and react with the acids at the O–H bond, leading to the formation of $CH_3C(=O)O\cdot$ and $CF_3C(=O)O\cdot$ radicals, which subsequently decompose readily. The final gaseous products were methane and trifluoromethane respectively. Energetically, however, the reaction of the benzoyl radical at the O–H bond in the acid is much less favourable than the reaction at the C–H bond. This anomalous behaviour of the benzoyl radical is due to the characteristic features of its structure, namely its ability to form a hydrogen bond with the hydroxyl hydrogen. This hydrogen bonding precedes the formation of the activated complex and facilitates the reaction.

Analogous effects were observed by Berezin and coworkers[17,18] in a study of the oxidative decarboxylation of acids. In these studies the rate of the reaction of peroxide radicals at the O–H bond in acids was found to be greater by a factor of 13 than the rate of their reaction at the C–H bonds, although energetically the first reaction is less favourable (by almost 12 kcal), so that its rate should have been less than that of the second reaction by a factor of almost 50. Here also, the unusual behaviour of the peroxide radical is apparently due to hydrogen bonding.

Although there are very few papers on the kinetic manifestation of hydrogen bonding involving radicals, there is no doubt that radicals take part in such bonding. Proof for this is provided by the large number of papers on the study of the EPR spectra of radicals in various solvents. It has been shown that the relaxation time and hyperfine splitting in the EPR spectra of radicals depends to a marked extent on the nature of the medium in which the radicals are found[48-52]. This effect is naturally due entirely to the properties of the medium and is regarded by a number of authors[52,54] as a solvation effect. Solvation alters the properties of the unpaired electron, its state, the distribution of its spin density, and hence the reactivity of the radical.

A simple model has been proposed[53] for the solvation of radicals. It was suggested that the changes in the splittings in the spectrum are due entirely to the redistribution of the π-electron spin density of the unpaired electron, and

that this density is influenced by the ligand which is solvating the radical and altering the electronegativity of the atom to which it is attached. Calculations by the molecular orbital method with allowance for the corresponding changes in the Coulomb integrals give the correct sign and magnitude for the observed effects.

Analysis of the EPR spectra of the nitrogen of the stable 2,2,6,6-tetramethylpiperidine *N*-oxide radical[55] showed that in solvating solvents (alcohol, water, or glycerol) the spin density of the unpaired π-electron on the nitrogen atom in the $>\dot{N}-O$ fragment increases by 3–4% relative to its value for inert solvents.

A detailed study of hydrogen bonding with the participation of an unpaired electron was made[56,57] for the example of aliphatic *N*-oxide radicals. It was shown that the changes in the EPR spectra are not related to the dielectric properties of the medium as a whole, but are due chiefly to hydrogen bonding. There is an increase in the constant for the isotropic splitting on the nitrogen as a result of the increase in spin density and possibly a change in bond hybridisation, leading to an increase in the proportion of the *s*-state in the wave function of the unpaired electron. There is a simultaneous decrease in the *g*-factor, the change showing a fairly good correlation with the displacement of the $n-\pi^*$ absorption band of the radical towards shorter wavelengths[58]. Thus the participation of the unpaired electron in hydrogen bonding leads to a significant change in its electronic state.

The same papers[56,57] describe a study of the dynamics of the equilibrium for the solvation of radicals according to the scheme: $R_0 + nS \overset{K}{\rightleftarrows} R_S$, where R_0 and R_S represent respectively "free" radicals and radicals solvated by molecules of the solvent S. The frequency of hydrogen bond formation and rupture was found to be much greater than the difference in the constants for the isotropic hyperfine interaction for the free and solvated radicals, that is the characteristic time required for equilibrium to be established is much less than 2×10^{-7} s. The value of the coordination number *n* for water is equal to unity, and the energies of the hydrogen bonds involving participation of the unpaired electron in the *N*-oxide radicals amount to 4 ± 2 kcal mole^{-1} on the average and do not differ greatly from the energies of ordinary hydrogen bonds. This apparently means that although the state of the unpaired electron in the hydrogen bond does indeed change, the main contribution to the bond energy is made by the donor–acceptor interaction of all the remaining electrons.

Hydrogen bonds involving other radicals, including intra-radical hydrogen bonds, have also been studied[57]. In none of these cases was it possible to obtain hyperfine splitting on the hydrogen atom taking part in hydrogen bonding, because of the short relaxation time for the solvation equilibrium. For strong hydrogen bonds, however, for example in the anion-radicals of naphthazarin and quinizarin[59] this splitting was apparently obtained. Further evidence of this was also provided by data on the scalar paramagnetic relaxation in NMR[60,61], associated with the appearance of an unpaired electron on the hydrogen atom in the hydrogen bridge; the constants for the hyperfine interaction on this hydrogen atom are about 10^4–10^6 s^{-1}. An interesting feature is that the paramagnetic oxygen molecule (triplet ground state) is also solvated by solvent molecules[62].

From the kinetic viewpoint, the formation of a hydrogen bond between the radical and the molecule with which it subsequently reacts may have two effects. Firstly, the formation of this complex may lead to an increase in the entropy of activation of the reaction, since the original state becomes a complex which subsequently undergoes monomolecular decomposition:

$$\dot{R} + HA \rightleftarrows \dot{R}\cdots H-A \rightarrow RH + \dot{A}.$$

Secondly, the participation of the unpaired electron in hydrogen bonding may lead to electronic perturbation of the reacting A–H bond in the complex $\dot{R}\ldots H-A$. Since the unpaired electron is delocalised over the A–H molecule, this complex as a whole can be regarded as a radical; it is possible that exchange or magnetic interactions play an important part in the complex. The idea of these interactions was put forward by McConnell[63] to explain the paramagnetic catalysis of polymerisation and *cis–trans* isomerisation. Berlin and Blyumenfel'd[64] developed this idea to explain the effects of "local activation". These ideas can also apparently be used in radical reactions. Here the reactivity of various radicals and molecules can be explained in terms of exchange interactions in the activated complex, the charge and spin densities at the reactive centre of the radical, etc. At least the kinetic manifestation of hydrogen bonding between radicals and reacting molecules can be readily explained on the basis of these ideas.

3. π-COMPLEXES IN RADICAL REACTIONS

In addition to the influence of hydrogen bonds, another characteristic feature of liquid-phase radical reactions is the influence of the aromaticity of the medium. This has been noted in many papers and is usually attributed to π-complex formation by the molecules and radicals.

According to Mulliken's classification[65], π-complexes are one of the forms of donor–acceptor complexes, in which the donors and acceptors are molecules with labile π-electron clouds (they are also called charge-transfer complexes — CTC). The main interaction in these complexes is between the filled electronic orbitals of the donor and the vacant orbitals of the acceptor.

π-Complexes have now been fairly well studied by physical methods. Electronic transitions between the filled orbitals of the donor and the vacant orbitals of the acceptor in the complex lead to the appearance of new absorption bands in the ultraviolet and visible range, so that spectrophotometry is most widely used to study the structure and properties of these complexes. Not only molecular complexes, but also complexes involving atoms[66–68] and radicals[69–71] have been studied.

The formation of π-complexes, leading to partial transfer of charge within the complex, should alter the electronic structure of the species and their reactivity. This effect should be shown particularly clearly in the kinetics of liquid-phase reactions, in view of the characteristic features of the liquid state.

There are extremely few papers devoted to the kinetic manifestation of π-complexes. We shall examine first π-complex formation by molecules taking part in reactions.

Alder and Leffler[72] observed that the aromaticity of the medium has a marked influence on the decomposition of phenylazotriphenylmethane. The values of the enthalpy and entropy of activation in various solvents were determined with high accuracy and it was shown that there is a linear relationship between them, that is a compensation effect is

observed. Aromatic solvents yield higher values for the enthalpy of activation and higher entropies, the increase in enthalpy on going from cyclohexane to aromatic solvents corresponding approximately to the heats of solvation of the molecules. This suggests that the activation of the decomposition requires preliminary desolvation. Evidence supporting this hypothesis was found by the authors[72] in the parallelism in the changes in the entropies of activation and entropies of fusion of the solvents. If we regard the breakdown of the π-complexes (desolvation) as fusion of the solvate sheath, this parallelism is readily understood. Thus the decomposition of the phenylazotriphenylmethane molecules to form radicals apparently involves consecutive desolvation and decomposition, but the participation of solvates in decomposition is not excluded.

A similar influence of the aromaticity of the medium was also observed in the decomposition of symmetrical diphenylazoethane and bisazomethylpropionitrile[73]. Ziegler did not observe these effects, however, for the decomposition of hexaphenylethane. This is apparently due to steric hindrance and the inability of the phenyl rings of hexaphenylethane to form π-complexes.

Let us now consider π-complex formation by atoms and radicals. Their ability to take part in π-complex formation with a donor is determined by their electrophilic nature (electron affinity) (see Table 2).

The problem of π-complexes involving an $R\dot{O}_2$ radical with a fairly high electron affinity has been very widely discussed for a long time. This discussion was begun in a paper by Boozer and Hammond[74] who put forward a mechanism for the inhibition of oxidation involving a π-complex of the peroxide radical:

$$R\dot{O}_2 + InH \rightleftarrows [RO_2^{\cdot}\cdots InH]$$
$$R\dot{O}_2\cdots InH] + R\dot{O}_2 \rightarrow ROOH + RO_2In.$$

This scheme was subsequently confirmed by Thomas[75] and Denisov[13]. Denisov made a detailed analysis of the conditions under which this mechanism should be revealed kinetically, and showed the limits of its influence.

Zaikov and coworkers[45], Ingold[76], and Russell[39], however, found that the dependence of the rate of oxidation on the dielectric constant of the medium obeys satisfactorily the Kirkwood–Onsager relationship, and no anomalies were observed for the rate of oxidation in aromatic media. Another extremely contradictory paper was published by Thomas[77], in which it was concluded that the $R\dot{O}_2$ radical forms a complex with trialkylamines. Direct experiments using the EPR method to detect π-complexes of the cumene peroxide radicals with a strong donor such as the pyridine molecule did not give positive results: the equilibrium for π-complex formation is displaced considerably towards the free radical[78], whereas even for the iodine molecule (electron affinity only 54.6 kcal mole^{-1}) the complexes with pyridine are extremely stable.

TABLE 2. Electron affinity of various radicals (kcal mole^{-1}).

Radical	Electron affinity	Radical	Electron affinity
$\dot{Cl}$	88.2	$\dot{O}H$	50
$\dot{F}$	83.5	$\dot{C}Rh_3$	48
$\dot{Br}$	81.6	$Ph\dot{O}$	27
$\dot{I}$	74.6	$\dot{C}H_3$	25
$H\dot{O}_2$	70		

Physically, it is extremely difficult to suppose that in the complex $[R\dot{O}_2\ldots InH]$ the interaction involves only π–π interaction and not hydrogen bonding. It might be possible to agree that a π-complex exists if it is assumed that the hydrogen bond between the peroxide radical and the inhibitor molecule InH is fairly weak, but there are as yet no serious grounds for this, rather the reverse: such bonds should be stable[36,37]. Thus at present it is fairly difficult to reach an unambiguous conclusion regarding the existence of π-complexes of $R\dot{O}_2$ with aromatic molecules.

All reactions involving the addition of atoms and radicals to aromatic systems with the formation of σ-complexes do of course involve the formation of intermediate π-complexes. This is apparently the case for the "attachment" of H atoms and $\dot{C}H_3$ radicals to aromatic molecules[79], phenylation[80], hydroxylation[81], and the reactions of peroxide radicals[82]. It is not always possible, however, to detect the intermediate π-complexes as kinetically independent species; this is determined chiefly by the competing reactions of decomposition of the π-complex and its conversion into the σ-complex.

π-Complex formation by the chlorine atom in the chain photochlorination of hydrocarbons has been studied in most detail by Russell[83–85]. In the chlorination of 2,3-dimethylbutane, isobutane, and other branched hydrocarbons the chlorine atom attacks the tertiary C–H bond only four times more readily than the primary bond. In the presence of aromatic solvents this rate ratio increases to 50–300, that is, tremendous selectivity is observed in the reactions of atomic chlorine. The dielectric properties of the medium are of almost no significance, and the order of selectivity (with respect to solvents) shows good correlation with the order of the basic strength of these solvents. This behaviour of the atoms cannot be attributed to the reactions of "hot" atoms and their "cooling" in the aromatic solvents, since the chlorination chains are fairly long, and almost no difference is observed in the rate constants for the gaseous and liquid phases. The most natural assumption is that the $\dot{Cl}$ atom forms a π-complex with the aromatic molecule and that this complex is much less reactive and hence more selective than the free atom. Analogous effects were observed by Russell[86] in the photochlorination of arylalkyl hydrocarbons.

To explain the regular kinetic features of photochlorination, Russell put forward a scheme involving the reaction of the free $\dot{Cl}$ atom and its π-complexes with coordination numbers x equal to one and two, and also π-complex formation equilibria between the $\dot{Cl}$ atoms and one or two aromatic molecules. This scheme does not show sufficiently good agreement with the experimental data[85]. Moreover, it is found that the heat of formation of the complex with x = = 2 is almost 4 times that for the complex with x = 1, which is physically unlikely. Despite the unsatisfactory kinetic analysis, however, there is no doubt that the π-complex is in fact formed and that its selectivity is high.

Berezin and coworkers[87] found that the aromaticity of the medium has a marked influence on hydrogen atom abstraction by the methyl radical from toluene and cyclohexane. The ratio of the rate constants for hydrogen atom abstraction from the aromatic molecule and from cyclohexane decreases sharply with increase in the concentration of benzene or toluene in the mixtures with cyclohexane. This effect at first sight reproduces qualitatively the results obtained by Russell, but it is much more difficult to interpret, since studies were made of the ratio of constants, each of which may depend in different ways on the aromaticity of the medium.

The lack of reactivity in the π-complexes of the t-butoxyl radical in reactions involving the removal of a hydrogen atom can apparently be attributed to the decrease in the ratio k_{subst}/k_{decomp} [see Eqns. (7) and (8)] in aromatic solvents[88-91].

Kinetic data on the influence of aromatic molecules on the rate of recombination of iodine atoms in the gaseous phase were examined by Porter and Smith[92] in terms of complexes with charge transfer between the iodine atoms and the aromatic molecules; the energies of these complexes amount to 1.7–2.4 kcal mole^{-1}. The formation of π-complexes between iodine atoms and hexamethylbenzene in the liquid phase in carbon tetrachloride has been proved spectrophotometrically and kinetically[93]; the equilibrium constant for π-complex formation at room temperature is 2.7 litre mole^{-1}.

A detailed study has been made of the π-complexes of stable aromatic N-oxide radicals and their kinetic manifestation in the removal of a hydrogen atom from 2,6-di-t-butylphenol, which is incapable of undergoing solvation[94]. It was first shown that the rate constants for the reaction of the diphenylnitrogen oxide radical with 2,6-di-t-butylphenol are much smaller in benzene and ethylbenzene than in heptane, the activation energies and pre-exponential terms increasing in the aromatic solvents. Analogous relationships were also observed for substituted diphenylnitrogen oxide radicals.

The kinetic scheme for the reaction of free nitrogen oxide radicals R_0 and their π-complexes R_S with 2,6-di-t-butylphenol PhOH can be represented in general form as follows:

$$\begin{gathered}\dot{R}_0 + PhOH \xrightarrow{k_0} RH + Ph\dot{O} \\ \dot{R}_S + PhOH \xrightarrow{k_S} RH + Ph\dot{O} \\ \dot{R}_0 + nS \underset{}{\overset{K}{\rightleftharpoons}} \dot{R}_S\end{gathered} \qquad (9)$$

where n, the coordination number of the π-complex, shows how many molecules of the solvent S must solvate the radical in order to produce a significant change in its reactivity. The scheme assumes reaction by the free radical and the π-complex, and also π-complex formation equilibrium. Analysis of scheme (9) leads to expression (I) for the effective rate constant k_{eff} for disappearance of the radicals. In an experimental investigation of the dependence of k_{eff} on [S], a study was made of the rate of disappearance of radicals in solvent mixtures, namely in benzene diluted with heptane[94]. The kinetic analysis is here similar to the analysis carried out for hydrogen bonding (see p. 194).

Fig. 3 shows the dependence of k_{eff} on [S] and its transformation into an equation similar to Eqn. (III) for the reaction of dianisylnitrogen oxide with 2,6-di-t-butylphenol at 60°; the value of n obtained from the slope of the straight line is equal to unity. Similar relationships were obtained for various temperatures. The equilibrium constant for π-complex formation by dianisylnitrogen oxide with benzene has the form

$$K = 3.3 \times 10^{-26} \exp(6400 \pm 2000/RT)\ cm^3. \qquad (10)$$

The numerical values of K obtained by the kinetic method show good agreement with the values of K obtained spectrophotometrically[95]; the energy of the bond in the π-complex, determined kinetically, coincides with the bond energy found independently from thermochemical data[96]. This confirms that the kinetic scheme (9) is correct.

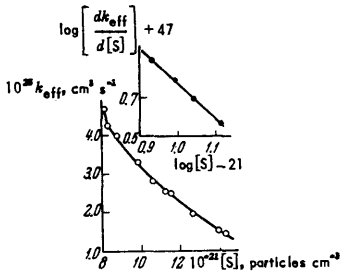


Fig. 3. Dependence of k_{eff} on the concentration of benzene in heptane and its logarithmic transform [according to Eqn. (III)] for the reaction of dianisylnitrogen oxide with di-t-butylphenol.[94]

It is extremely significant that the values of k_S are smaller by an order of magnitude than the values of k_0, that is the π-complex is much less reactive than the free radical; for kinetics, the association of the radical with only one solvent molecule (n = 1) is significant. Further association and further growth of the solvate sheath have no significance, apparently because the first solvating molecule produces the greatest perturbation in the electronic structure of the radical.

The removal of a hydrogen atom from ethylbenzene by various stable N-oxide radicals has been studied[97]. For the reaction of dianisylnitrogen oxide with ethylbenzene, the rate constant increases when the ethylbenzene is diluted with n-decane. This means that the π-complex of the radical with ethylbenzene has a low activity, and no reaction takes place within the complex. This confirms the analogous conclusion reached by Russell[83] for the Cl atom in a π-complex.

The low reactivity of the π-complex is not a general feature. It has been shown[94] that the π-complexes of dianisylnitrogen oxide with pyridine and its derivatives have a high reactivity and react with a smaller activation energy than the free radical. This effect is not due to the influence of the dielectric constant of the medium, since in dichloroethane, whose dielectric constant ϵ is close to that of pyridine, the rate constants and activation energies are almost the same as those in heptane. Thus the reactivity of the π-complex may depend on whether the radical behaves as a donor or an acceptor in the complex.

The problem of whether electron transfer in the π-complex of the radical involves the unpaired electron or includes other lower-lying electrons is of particular interest. Direct measurements, by the NMR method, of the constants for the hyperfine splitting due to delocalisation of the unpaired electron on the molecules of the medium solvating the radical showed that if such delocalisation does in fact take place, it is extremely slight[99]. Studies of the dynamic nuclear polarisation on a number of radicals in aromatic solvents also showed that the degree of delocalisation of the unpaired electron on the ligand in the π-complex is extremely slight[100-102]. There is apparently only slight transfer of charge in the π-complex. The kinetic effects produced by this transfer are fairly large, however.

A compensation effect was observed[97] in the removal of a hydrogen atom from ethylbenzene by aromatic N-oxide radicals. The fact that the radicals for which this effect was observed have extremely similar structures makes it

impossible to attribute the effect to structural differences in the radicals. The origin of the compensation effect must therefore be sought not in the reactivity of the radicals themselves, but in their specific interactions with the medium.

It is apparently a general feature that the compensation effect in liquid-phase radical reactions is usually not observed when the reaction is in fact an elementary reaction. When the reaction is complicated by specific interactions between the reacting species and the solvent molecules (hydrogen bonding, π-complexes), the compensation effect is usually observed. It can be shown that the compensation effect is to be expected when the measured kinetic constants are made up of the rate constants for a number of elementary acts[98].

4. POLAR FACTORS AND SPECIFIC INTERACTIONS IN RADICAL LIQUID-PHASE REACTIONS

As noted above, contradictory experimental facts have been published on the kinetic manifestation of polar factors associated with electrostatic dipole–dipole interactions between the reacting species.

It has been shown in a whole series of papers that the dielectric constant of the solvent has a marked influence on the rate of the radical reactions involved in the oxidation of ethanol and methyl ethyl ketone[45,46,103,104], and alkenes and arylalkyl hydrocarbons[39,76,105], and also the rate of decomposition of t-butyl peroxyformate[106]. In all these examples, the dependence of the reaction rate on the dielectric constant obeys the Kirkwood–Onsager relationship and indicates that the dipolar character of the transition state in these reactions is greater than the dipolar character of the initial reagents.

The dielectric constant of the solvent has absolutely no influence, however, on the rates of the reactions of chlorine atoms with hydrocarbons[85], or of phenoxyl and N-oxide radicals with phenols[24,94], or on the rate of the copolymerisation of styrene with methyl methacrylate or of α-methylstyrene with maleic anhydride[107,108], where it would seem that the strongest polar effects should be revealed. In these examples, as shown above, an important part is played by specific localised interations of the donor–acceptor type.

The latter influence chiefly the initial state of the system, whereas the polar factors exert their chief influence on the activated complex of the reaction. The greater or lesser part played by the polar factors is apparently determined by the electronic structure of the activated complex. The course of the radical reaction $\dot{R} + HX \rightarrow RH + \dot{X}$ can in fact be represented by two schemes:

$$\dot{R} + HX \begin{cases} \xrightarrow{(1)} [\dot{R}\cdots H\cdots X] \rightarrow RH + \dot{X} \\ \xrightarrow{(2)} [R^{(-)}\overset{(+)}{H}X] \rightarrow R^- + H^+ + \dot{X} \rightarrow RH + \dot{X}. \end{cases}$$

Route (1) involves the slow movement of a proton from X to R in the potential field created by rapid electronic motion. Route (2) assumes the transfer of charge from HX to R with the formation of R^- and the cation-radical $\dot{HX}$, which subsequently decomposes to a proton and the radical $\dot{X}$. This reaction path assumes that the charges in the activated complex are separated in time and space; a consequence of this separation is the polarisation of the activated complex and the dependence of the rate on the dielectric constant. The fundamental difference between these routes is that in one case the limiting stage involves the movements of nuclei whereas in the other case electron transfer takes place. Route (2) naturally does not require complete transfer of the electron in the activated complex; only partial transfer, with partial charge separation in the complex, is sufficient.

The realisation of a given form of activated complex depends on the polarity of the medium, which either facilitates the separation of charges or hinders it, and also on the properties of the reacting species — the ionisation potential of the molecule HX and the electron affinity of the radical $\dot{R}$.

This interpretation of the form of the activated complex enables us to look for the possibility of acid–base catalysis of radical reactions. It has in fact been possible to observe examples of both base catalysis (the decomposition of t-butyl peroxyformate in the presence of pyridine)[106] and acid catalysis[109].

Thus the relative part played by polar factors and specific interactions is determined by the form of the activated complex, and its electronic structure.

In conclusion it should be noted that the study of specific localised interactions and polar factors and the part which they play in the kinetics of radical liquid-phase reactions is enriching considerably our knowledge of electronic interactions in the activated complex. The need for further intensive studies in this direction and their undoubted success are obvious.

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THE CHEMISTRY OF HOT HYDROGEN ATOMS WITH 1-3 eV ENERGY AND OF EXCITED RADICALS

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I. INTRODUCTION

Many investigations [1-10] of the chemistry of hot tritium atoms produced by the nuclear reactions $^6Li(n,\alpha)T$ and $^3He(n,p)T$ (recoil energy of the T atoms 2.7 and 0.2 MeV respectively) have shown that these atoms can efficiently take part in chemical reactions when slowed down to energies comparable to those of chemical interaction: in particular, they can take part in transfer and substitution reactions proceeding without activation energy

$$T^* + RH \rightarrow HT + R^\cdot \quad (1)$$
$$T^* + RH \rightarrow RT + H \quad (2)$$

For thermal hydrogen atoms the activation energy of reaction (1) is 9-12 kcal mole^{-1}; reaction (2) is not known to occur with thermal H atoms.

Hot T atoms can add on to the double bond of alkenes, giving excited radicals [6,10], and they can also replace individual atoms or even groups of atoms in complicated molecules [1,7]: when this happens the intermediate products can be used in an excited state, and the decomposition mechanisms will be determined by a number of factors (degree of excitation, efficiency of transfer of the excitation energy, etc. [7,8]).

It should be noted that the formation of fast atoms and of excited molecules and radicals is not confined to processes accompanying nuclear transmutations, but it occurs also in radiolysis, photolysis, and even in thermal reactions at high temperatures.

To explain various anomalies in the behaviour of atoms and radicals, many workers in the field of kinetics have put forward the concept of an abnormally high reactivity for the hot hydrogen atoms and radicals obtained in the radiolysis of hydrocarbons and in the photolytic decomposition of excited molecules.

The majority of workers believe that the primary act in the radiolysis of hydrocarbons is fissure of the C-H bond.

The energy excess $E_{excit} - D_{C-H}$ (where D is the dissociation energy of the C-H bond) apportions itself between R and H in inverse proportion to the masses, and is carried away mainly in the form of kinetic energy by the H atom [11].

Hot H* atoms with a kinetic energy of the order of several electron-volts are reactive at low temperatures as well as at ordinary temperatures [12-14]. Armstrong [14] has demonstrated experimentally the existence of hot hydrogen atoms in his study of the low-temperature radiolysis of HCl at -78° and -196°. These atoms are produced by the decomposition of an excited HCl* molecule ($HCl^+ + e \rightarrow HCl^* \rightarrow H^* + Cl$). Radiation yields G of 4.0 and 2.4 respectively were measured for the formation of hot and of thermal H atoms.

The concept of hot H* atoms has been invoked many times in work on the liquid-phase and gas-phase radiolysis of hydrocarbons [15-17]. Reactions between highly excited H* atoms and C_2H_4 molecules have also been detected mass-spectrometrically [18].

However, a quantitative interpretation of reaction schemes involving hot atoms during radiolysis presents serious difficulties, because of the presence of various competing reactions, of the unknown energy spectrum of the hot atoms, etc.

The most convenient route for the preparation of H* atoms is through photochemical reactions, in particular the photodissociation of the hydrogen halides HI and HBr.

II. FORMATION OF HOT HYDROGEN ATOMS DURING PHOTOLYSIS OF HI AND HBr, AND THEIR REACTIONS

Kondrat'ev and coworkers had shown [19], as long ago as in 1934, that the reactivity of H atoms obtained by the photolysis of HI is essentially dependent on their kinetic energy.

Hydrogen iodide has a continuous absorption spectrum in the ultraviolet region, beginning at 3850 Å. [20,21] The maximum extinction coefficient ϵ lies in the region of 2500 Å, and has a value of $\sim 2 \times 10^{-19}$ cm^2 per molecule [20]. Since ϵ_{HI} is high in the region of 2500 Å, and most of the radiation with λ = 2537 Å is absorbed in the first centimeter of optical path at atmospheric pressure, the experiments are usually made at lower HI pressures (~ 10-30 mmHg).

The most commonly used sources of ultraviolet radiation are low-pressure cadmium or mercury resonance lamps of type Hanovia SC 2537 (or lamps type PRK-2 or PKR-4, made in the Soviet Union). For experiments at λ = 1849 Å these lamps are fitted with a Suprasil window [22,23], and with a filter of lithium fluoride irradiated with X-rays or γ-rays,

which transmits ~ 50% of the light with λ = 1849 Å but almost completely suppresses the light of wavelength λ = 2537 Å.

The H* atoms formed in the photolytic decomposition of HI* have a kinetic energy of

$$E_{H^*} = [E_{h\nu} - D_{HI} - E_{I^*}] \times \frac{127}{128} \quad (I)$$

where $E_{h\nu}$ is the energy of the impinging quantum, D_{HI} the dissociation energy of HI, equal to 71 kcal mole^{-1}, and E_{I^*} the electronic excitation energy of an iodine atom to the $I^2P_{1/2}$ state, equal[24] to 21.8 kcal mole^{-1}. Thus, for λ = 3130, 2537, and 1849 Å the energy of hot H* atoms is 20, 41, and 82 kcal mole^{-1} respectively (0.9, 1.8, and 3.6 eV) if the I atom is in the $I^2P_{3/2}$ ground state.

During photolysis of HBr the spectrum of the first formed H* atoms lies in a narrower range of energies, because the first excited state of the bromine atom is 0.4 eV above the ground state[22,24]. In the photolysis of HBr the energy of tne H* atoms is lower than in the photolysis of HI (since the mass of Br is smaller than that of I), and hence the spectrum of H* atoms is narrower and lies in the range 2.5–2.9 eV at λ = 1849 Å. The use of HBr for the production of H* atoms with ~ 3 eV energy also has some other advantages as compared with HI: 1) HBr absorbs weakly in the region of λ = 2537 Å, so that photolysis can be carried out without a filter; 2) the extinction coefficient of Br_2 at λ = 1849 Å is considerably lower than that of I_2; 3) HBr is chemically more stable than HI.

The quantum yield of hydrogen, Φ_{H_2}, during photolysis of HI in the region of λ ≃ 2500 Å is unity, and is independent of temperature between -78° [23] and 190°.[25] The temperature independence of Φ_{H_2} can be explained by a reaction scheme involving hot H* atoms:

$$HI \xrightarrow{h\nu} H^* + I(^2P_{1/2} \text{ or } {}^2P_{3/2}) \quad (3)$$
$$H^* + HI \rightarrow H_2 + I \quad (4)$$
$$H^* + I_2 \rightarrow HI + I \quad (5)$$
$$I + I + M \rightarrow I_2 + M. \quad (6)$$

Chain branching does not take place, because the reaction

$$I + HI \rightarrow I_2 + H \quad (7)$$

is endothermic by 35 kcal mole^{-1}. It has been shown[26] that even $I^2P_{1/2}$ atoms hardly ever undergo transfer reactions of the type (7). The steady-state rate of formation of H_2 and I_2 is

$$\frac{d(H_2)}{dt} = \frac{d(I_2)}{dt} = \frac{I_a}{1 + \frac{k_5}{k_4}\frac{(I_2)}{(HI)}} \quad (II)$$

where I_a is the number of photons absorbed in 1 sec. At low extents of reaction, when the ratio I_2/HI can be treated as constant, the quantum yield of hydrogen Φ_{H_2} is

$$\Phi_{H_2} = \frac{(H_2)_{fin} - (H_2)_{init}}{\int_0^t I_a\,dt} \simeq \frac{1}{1 + \frac{k_5}{k_4}\frac{(I_2)}{(HI)}}. \quad (III)$$

It is evident from Eqn. (III) that $1/\Phi_{H_2}$ is a linear function of the ratio I_2/HI, whose slope gives the ratio k_5/k_4. Schwarz and coworkers[27] examined the photolysis of HI at λ = 2537 Å and found that the ratio k_5/k_4 is 3.8 and does not vary with temperature. Addition of inert moderators (Ne, Ar, He, etc.) results[25] in a decrease of k_4/k_5 from 0.25 to 0.014, and an activation energy $E_4 - E_5 = 4.5 \pm 0.8$ kcal mole^{-1} appears[27].

These results on the effect of temperature and of added inert moderators are difficult to explain in terms of classical kinetics unless the concept of hot atoms is adopted. Thus, the temperature independence of Φ_{H_2} is readily explained if the enhanced reactivity of hot H* atoms is ascribed to the excess kinetic energy of these atoms, which is higher than or equal to the threshold energy required for any particular reaction. The addition of inert moderators to the system causes thermalisation of the hot H* atoms. If we assume that inhibition involves an elastic collision mechanism, the average energy loss per collision, $\Delta\overline{E}/E$, is

$$\frac{\Delta\overline{E}}{E} = \frac{2m_1m_2}{(m_1+m_2)^2} \quad (IV)$$

where m_1 and m_2 are the masses of the colliding atoms. $\Delta\overline{E}/E$ reaches a maximum for $m_1 = m_2$, and therefore He is a more efficient moderator than Ar. The slowing down of H* on HI molecules is a slow process. If He is added, however, the slowing down of H* atoms becomes fast, the probability of reaction (4) decreases, and the ratio k_4/k_5 also decreases. Further experimental confirmation of the reactions of hot H* atoms formed in the photolysis of HI and HBr can be found in the papers of Martin and Willard[22,23] and by Carter and coworkers[28] on the photolysis of HI–RH and HBr–RH mixtures and of their deuterated derivatives at λ = 2537 and 1849 Å, where RH = H_2, CH_4, C_2H_6, C_5H_{12}.

In this case, in addition to reactions (3)–(6), the following reactions occur:

$$D^* + DI \rightarrow D_2 + I \quad (8)$$
$$D^* + RH \rightarrow HD + R^\cdot \quad (9)$$
$$D^* + DI \rightarrow D + DI \quad (10)$$
$$D^* + RH \rightarrow D + RH \quad (11)$$
$$D^* + M \rightarrow D + M \quad (12)$$
$$D + DI \rightarrow D_2 + I \quad (13)$$
$$D + RH \rightarrow HD + R^\cdot \quad (14)$$
$$R + DI \rightarrow RD + I \quad (15)$$

where D* is a hot deuterium atom and D is a slowed deuterium atom. Since the activation energy of (14) is large (~ 7–12 kcal mole^{-1} for thermal hydrogen atoms), it may be assumed that at high concentrations of RH the formation of HD occurs mainly by reaction (9). Then

$$\frac{D_2}{HD} = \frac{k_8}{k_9}\frac{[DI]}{[RH]} + \frac{k_{11}}{k_9} + \frac{k_{12}}{k_9}\frac{[M]}{[RH]} \quad (V)$$

and in the absence of the moderator M we have the linear relationship

$$\frac{D_2}{HD} = \frac{k_8}{k_9}\frac{[DI]}{[RH]} + \frac{k_{11}}{k_9}. \quad (VI)$$

The intercept on the y-axis of the plot of D_2/HD against DI/RH corresponds to k_{11}/k_9, and the slope corresponds to k_8/k_9.

From the slope and the intercept we can, with appropriate assumptions, evaluate the mean probability of reaction per collision in the hot region and the mean energy loss per collision with a hydrocarbon molecule during the thermalisation. Table 1 gives the results of Carter and coworkers[28] and of Martin and Willard[22] for k_8/k_9 and k_{11}/k_9 in the photolysis of DI–RH and HBr(DBr)–RH(RD) mixtures, and also the mean reaction probabilities per collision and the mean energy losses per collision.

The increase of the D_2/HD ratio with increase of wavelength λ, or with addition of an inert moderator, as well as the lack of temperature dependence, is evidence that hot H* atom reactions occur during photolysis of HI.

TABLE 1. Efficiency of slowing down and probability of hot reactions in the DI–RH and HBr(DBr)–RH(RD) systems.[22,27]

λ, Å	System	Fraction of atoms slowed down	Fraction of atoms reacting with hot atoms	k_0/k_0	k_{11}/k_0	Average reaction probability per collision		Average loss of energy per collision		Reference
						P_s	P_0	f_{tot}	$f_{elastic}$	
2537	DI–H_2	0.58	0.42	5.64	1.40					
	DI–C_2H_6	0 81	0.19	6.40	4.33					27
	DI–CH_4	0.94	0.057	24.3	16 7					
	DI–C_5H_{12}	—	—	4.65	4.80					
1849	HBr–D_2	0.39	0.61	2.04	0.65	0.26	0.17	0.32	0.32	22
	HBr–CD_4	0.94	0.062	81	15		0.0031	0.07	0.091	
	HBr–C_2D_6	0.86	0.14	11.8	6.1		0.018	0.19	0.052	
	DBr–H_2	0.38	0.62	1.54	0.60	0.41	0.35	0.50	0.50	
	DBr–CH_4	0.83	0.17	6.40	5.0		0.002	0.42	0.20	22
	DBr–C_2H_6	0.69	0.31	2.25	2.2		0.14	0.51	0.12	

As the kinetic energy of the H* atom increases, the role of "hot" reactions becomes more important. Thus, in the case of CH_4 and C_2H_6, the fraction of "hot" reactions by hydrogen atoms increases from 6 to 17 and from 19 to 31% respectively as the energy of the H* atoms is raised from 0.9–1.8 eV (λ = 2437 Å) to 2.5–2.9 eV (λ = 1849 Å). The ratio k_1/k_2 for hot T* atoms of energy ~ 3 eV is 3.5–4, as shown[9] by a study of the photolysis of TBr (λ = 1849 Å) mixed with CH_4 and C_2H_6. With tritium recoil atoms having an initial energy of 0.2 MeV, the "hot" reactions (1) and (2) account for 50–70% of the total amount of tritium atoms consumed[1–10].

Hot H* atoms obtained by the photolytic decomposition of HI have an enhanced reactivity, since they can bring about replacement reactions not only at room temperature (in the gas[19,23,28] and in the liquid phase[29,31]) but also, in the solid phase, at temperatures of -78°[22,31] and -196°,[30] as shown for the low-temperature photolysis of HI (0.01–0.1 mole %) in a matrix of 3-methylpentane. The quantum yield Φ_{H^*} is 0.2 in the liquid phase at 298°K and in the solid phase at 123°K; $\Phi_{H_{thermal}}$ = 0.8 at 298°K, falling to 0.2 at 77°K.

With thermal H atoms, low-temperature replacement reactions are effectively excluded by the large activation energy.

III. FORMATION AND REACTIONS OF EXCITED RADICALS OBTAINED BY PHOTOLYSIS OF ALKYL HALIDES AND OTHER COMPOUNDS

Radiolytic and photolytic processes can give rise not only to hot hydrogen atoms having an excess of kinetic energy, but also to "hot" vibrationally excited radicals whose reactivity increases markedly with the energy of the source of excitation.

The reactions of "hot" radicals obtained in the photolysis of alkyl iodides have been most fully investigated. Alkyl iodides have a continuous absorption spectrum in the region 2500–2600 Å. When an excited molecule of alkyl iodide decomposes, the energy excess $E_{h\nu} - D_{R-I}$ apportions itself among the residues in inverse proportion to their masses. For example, in the photolysis of CH_3I at λ = 2537 Å ($E_{h\nu}$ = 112 kcal mole^{-1}), $E_{h\nu} - D_{CH_3-I}$ equals 57 kcal mole^{-1} if I is in the $I^2P_{3/2}$ state and 35 kcal mole^{-1} if I is in the $I^2P_{1/2}$ state. Since the masses of CH_3 and I are very different, ~ 7/8 of this energy will be imparted to the CH_3 radical, and as a result the latter will become vibrationally excited.

Many papers[32–40] give experimental proof of the higher reactivity of vibrationally excited CH_3^* radicals as compared with thermal CH_3 radicals.

One usually considers the following scheme during photolysis of CH_3I:

$$CH_3I \xrightarrow{h\nu} CH_3^* + I \quad (16)$$

$$CH_3^* + CH_3I \longrightarrow CH_4 + CH_2I \quad (17)$$

$$CH_3^* + RH \longrightarrow CH_4 + R^\cdot \quad (18)$$

$$CH_3^* + CH_3I \longrightarrow C_2H_6 + I \quad (19)$$

$$CH_3^* + CH_3I \longrightarrow CH_3 + CH_3I \quad (20)$$

$$CH_3^* + M \longrightarrow CH_3 + M \quad (21)$$

and also the recombination reactions of thermal CH_3 and CH_2I radicals and I_2 addition reactions. It has been shown that the main reactions of the CH_3^* radical are the abstraction reactions (17) and (18), the rate of formation of CH_4 being unaffected by temperature over the range from -78° to 300°, whereas additions of inhibitors (I_2, O_2, NO) and of inert moderators (noble gases, N_2, CO_2) lower the rate of formation of CH_4.[36,38]

Reactions (17) and (18) are observed not only in the gaseous and in the liquid phase, but also in the solid phase at low temperatures. Formation of CH_4 has been reported at a temperature of 4°K in pure CH_3I,[39] at 77°K in hydrocarbon matrices[40,41], and at 20°K in solid inert matrices of Kr, Xe, and N_2 containing C_2H_6 and $(CH_3)_3CH$.[42] On changing from the liquid to the solid phase Φ_{CH_4} decreases by approximately a factor of 5–7, the decrease taking the form of a discontinuity at the phase transition point[40].

The decrease in Φ_{CH_4} on going over to the solid phase may be due to greater efficiency of the deactivation processes experienced by the CH_3^* radicals in the solid phase.

It is important to note that during solid-phase photolysis (77°K) of CH_3I and of solutions of CH_3I and CD_3I in methylcyclohexane, stabilisation of the CH_3^* radicals cannot occur to any significant extent[40,42]: only R· radicals formed by reactions (17) and (18) were detected by the ESR method.

On the other hand, partial stabilisation of the methyl radicals occurs in the photolysis of azomethane, since in this case the proportion of hot CH_3^* radicals (produced by the decomposition of the excited $CH_3-N=N-CH_3^*$ molecule) is not large.

The reactivity of CH_3^* increases with the excitation energy. Thus, Φ_{CH_4} values of 0.15×10^{-3}, 3.2×10^{-3}, and 30×10^{-3} have been reported[38] for the photolysis of CH_3I with light of λ = 3130, 2537, and 1849 Å respectively.

It is also found that the probability of the "hot" reaction (19) increases with the excitation energy, as shown by experiments on the influence of added inhibitors and inert moderators on the yield of C_2H_6.

The formation of "hot" $C_2H_5^*$ radicals during photolysis of C_2H_5I (λ = 2537 Å) in the liquid and in the solid phase was demonstrated by Luebbe and Willard[43] in spite of the much lower excitation energy of $C_2H_5^*$ as compared with CH_3^* (a consequence of the greater mass of the C_2H_5 radical).

"Hot" radicals appear also in various other photochemical processes. Thus, the flash photolysis of azo-

methane (λ = 3000–4000 Å) can give CH_3^* radicals in the primary act:

$$CH_3{-}N{=}N{-}CH_3^* \rightarrow N_2 + 2CH_3^* \quad (22)$$

followed by extraction of hydrogen from the neopentane present in the system as a second component:

$$CH_3^* + RH \rightarrow CH_4 + R^* \quad (23)$$
$$CH_3 + CH_3 \rightarrow C_2H_6. \quad (24)$$

The proportion of CH_3^* in this case is not large (~ 1% of the total number of CH_3 radicals formed), as shown by the low (~ 0.03) ratio of CH_4/C_2H_6.[40,43] When λ is increased from 3000 to 4000 Å this ratio decreases[43] by a further factor of 3–4. The lower yield of CH_3^* radicals in azomethane as compared with CH_3I is due to the fact that two bonds are broken when $CH_3{-}N{=}N{-}CH_3^*$ decomposes, and the energy excess is divided among at least three particles.

Several hot particles can form when the quantum energy of the incident light is increased. Thus, the photolysis of acetone in the vacuum ultraviolet region (λ = 1236 and 1470 Å) can result in the simultaneous production of CH_3^* radicals and hot hydrogen atoms[44]. The formation of hot acetyl radicals during the photolysis of ketones at λ = 2537 Å has been reported[45].

Several workers have shown[46,47] that the photolysis of diethyl ketone (λ = 2200–3100 Å) produces "hot" propionyl radicals $CH_3CH_2CO^*$ which subsequently decompose into C_2H_4, CO, and H. Hot halomethyl radicals produced in the photolysis of halomethanes also show enhanced reactivity towards displacement reactions[48].

The possibility of forming vibrationally excited radicals has been demonstrated, in the case of the photolysis of azoethane $(C_2H_5)_2N_2$, by changing from 3600 to 2300 Å.[49]

IV. FORMATION OF VIBRATIONALLY EXCITED ALKYL RADICALS BY THE ADDITION OF ATOMIC HYDROGEN TO ALKENES

"Hot" radicals can be obtained not only in photochemical processes and in radiolysis, but also in ordinary chemical reactions. The heat attending the addition of H atoms to C=C bonds is known to be ~ 40 kcal mole^{-1}. This reaction gives rise to vib.ationally excited alkyl radicals, which can decompose in the absence of stabilising collisions or extract hydrogen from RH, as was reported[50–52] for "hot" $C_3H_7^*$ radicals:

$$C_3H_7^* \rightarrow C_2H_4 + CH_3 \quad (25)$$
$$C_3H_7^* + H_2 \rightarrow C_3H_8 + H \quad (26)$$
$$C_3H_7^* + C_3H_6 \rightarrow C_3H_8 + C_3H_5^*. \quad (27)$$

The rate of decomposition of $C_3H_7^*$ depends on the structure of the radical: for n-$C_3H_7^*$ the rate of decomposition is 100–1000 times higher than for iso-$C_3H_7^*$. When H atoms add on to alkenes of higher molecular weight, the number of possible decomposition routes for the "hot" radicals increases. Thus, for $C_4H_9^*$ radicals two decomposition paths are possible[53]:

$$C_4H_9^* \rightarrow CH_3^* + C_3H_6 \quad (28)$$
$$C_4H_9^* \rightarrow C_2H_5^* + C_2H_4. \quad (29)$$

The decomposition constant of the $C_4H_9^*$ radical at 305°K is independent of pressure[54] over the range 0.036–115 atm.

A great deal of work has been done on the reactivity of vibrationally excited $C_2H_5^*$ radicals obtained by the reaction

$$H + C_2H_4 \rightarrow C_2H_{5vibr}. \quad (30)$$

We know from chemical kinetics that the basic reactions of thermal ethyl radicals obtained by the photolysis of diethylketone[55–57], acetaldehyde[58,59], azoethane[49,60], etc. are recombination and disproportionation reactions:

$$C_2H_5^* + C_2H_5^* \rightarrow C_4H_{10} \quad (31)$$
$$C_2H_5^* + C_2H_5^* \rightarrow C_2H_6 + C_2H_4 \quad (32)$$

with k_{32}/k_{31} = 0.1–0.2, and $E_{32} - E_{31}$ = 0.8 ± 0.2 kcal × × mole^{-1}.[61] If, however, the ethyl radicals are obtained in a vibrationally excited state by the addition of H atoms to C_2H_4 — mercury photosensitised Hg6($^3P_1$) decomposition of C_2H_4, etc. — the ratio k_{32}/k_{31} increases, but the scatter of experimental results is quite large (from 0.1 to 0.8) and the ratio depends on various factors such as the pressure in the system, the intensity of irradiation, the amount of mercury, the presence of inert additives, etc.[62–66]

The increased yield of C_2H_6 has been explained in various ways. It is suggested that vibrationally excited $C_2H_5^*$ radicals undergo disproportionation reactions more readily than thermal C_2H_5 radicals[65], and that they are able to extract hydrogen[64], but a unified point of view on this problem is still lacking. $C_2H_5^*$ radicals are relatively long-lived, and can experience up to 10^4–10^6 collisions before becoming thermalised, the efficiency of slowing down of $C_2H_5^*$ on C_2H_4, H_2, He, Ne, etc. showing large differences.

Current, Cvetanovich, Rabinovitch, and others[67–70] have made detailed studies of the stabilisation and decomposition of vibrationally excited ethyl radicals obtained by adding H and D atoms to C_2D_4 and C_2H_4. They postulated the reactions

$$C_2H_4 + D \rightleftarrows C_2H_4D^* \quad (33)$$
$$C_2H_4D^* \rightarrow C_2H_3D + H \quad (34)$$
$$C_2H_4D^* + M \rightarrow C_2H_4D + M. \quad (35)$$

The influence of pressure (0.05–3 mmHg) and temperature in the range from -78° to 160° on the ratio k_{35}/k_{34} was investigated, and the experimental results were analysed by Kassel's theory. It was shown that k_{34} is relatively insensitive to temperature, varying from 2.5 × 10^7 to 6.5 × × 10^7 s^{-1} between 195° and 300°K in the case of the $C_2H_2D_3$ radical. The ratio k_{35}/k_{34} is likewise insensitive to temperature, having the values 3.0 and 2.0 at 195° and 300°K respectively for $C_2H_2D_3$. However, a large isotope effect was noted in reactions (34) and (35): thus, for the $C_2H_3D_2^*$ radical under the same conditions k_{35}/k_{34} was 18 and 6.3 at 195° and 300°K respectively, i.e. significantly higher than for the $C_2H_2D_3^*$ radical[67].

It should be noted that vibrationally excited radicals can also be produced in reactions other than the addition of H atoms to alkenes (for example, in polymerisation[71] or in the addition of oxygen or halogen atoms to the C=C bond[72]). Studies of the reactivity of such radicals are very valuable in understanding a number of important processes (hydrocarbon oxidation, halogenation, etc.).

V. REACTIONS BETWEEN HOT H* ATOMS OBTAINED BY PHOTOLYSIS OF HI AND ETHYLENE

A great deal of work has been devoted to the study of the reactivity towards alkanes of hot H* atoms obtained in the photolytic decomposition of HI, but very little information

exists on the interaction between hot hydrogen atoms and alkenes. Yet, this problem is clearly very relevant from the point of view of explaining the influence of the kinetic energy of the H* atoms on the degree of excitation and on the reactivity of the resulting alkyl radical. Studies of the reactions of tritium recoil atoms have shown that alkenes can undergo not only extraction and substitution reactions, as in the case of alkanes, but also addition of a hot hydrogen atom to the double bond with formation of excited radicals [73] which subsequently decompose:

$$T + CH_3(CH_2)_2CH=CHCH_3 \rightarrow CH_3(CH_2)_3\dot{C}HTCHCH_3 \rightarrow CHT=CHCH_3 + CH_3(CH_2)_2. \quad (36)$$

The decomposition of excited radicals is a unimolecular process, analogous to the decomposition of the vibrationally excited radicals obtained by the addition of thermal hydrogen atoms to alkenes [53]. Lee and Rowland [6] have shown that the probability of stabilisation of excited radicals in a condensed phase at low temperatures is higher than in the gas phase

$$T^* + CH_3-CH=CH-CH_3 \rightarrow (CH_3-\dot{C}H-CHT-CH_3)^* \quad (37)$$

$$(CH_3-\dot{C}H-CHT-CH_3)^* \xrightarrow{RH} CH_3CH_2CHT-CH_3 \quad (38)$$

$$(CH_3-\dot{C}H-CHT-CH_3)^* \rightarrow CH_3CH=CHT+CH_3 \quad (39)$$

There is an almost complete lack of data on the reactions of hot H* atoms obtained by the photolysis of HI with alkenes. A systematic study of the reactions between hot H* atoms with 0.9–1.8 eV energy and ethylene was carried out in the Nuclear and Radiation Chemistry laboratory of the Institute of Chemical Physics of the Academy of Sciences of the USSR. The results have been partially reported in a number of papers [74-76]. Photolysis (λ = 2537 Å) of HI–C_2H_4 mixtures was found to give C_2H_6 and H_2 as the main products: butane and other hydrocarbons were not detected. The rate of formation of ethane ($W_{C_2H_6}$) is independent of temperature over a wide range (0–250°). Additions of inert moderators (helium and argon) affect $W_{C_2H_6}$ in different ways: argon has no effect, but helium causes a decrease in $W_{C_2H_6}$. The results are difficult to explain in terms of conventional kinetics. Let us consider the probable reaction scheme in the C_2H_4–HI system. Since C_2H_4 does not absorb in the 2500 Å region, the decomposition of HI with formation of a hot H* atom and an I atom is the only possible primary process resulting from photon absorption:

$$HI \xrightarrow{h\nu} HI^* \rightarrow H^* + I(^2P_{1/2} \text{ or } ^2P_{3/2}). \quad (40)$$

Hot H* atoms with 0.9–1.8 eV energy can undergo an abstraction reaction

$$H^* + HI \rightarrow H_2 + I \quad (41)$$

$$H^* + C_2H_4 \rightarrow H_2 + C_2H_3^\cdot \quad (42)$$

or they can become thermalised

$$H^* + HI \rightarrow H + I \quad (43)$$

$$H^* + C_2H_4 \rightarrow H + C_2H_4. \quad (44)$$

Thermal H atoms will, on the whole, add to the C=C bond, because abstraction from RH involves a large activation energy (~ 7–12 kcal mole^{-1}):

$$H + C_2H_4 \rightarrow H + C_2H_5\,{}_{vibr}. \quad (45)$$

Vibrationally excited C_2H_5 radicals dissociate into H and C_2H_4, or become thermalised. Thermal C_2H_5 radicals can recombine, disproportionate, be captured by I_2, or combine at the C=C bond (thus creating a polymerisation chain):

$$C_2H^\cdot + C_2H_5^\cdot \rightarrow C_4H_{10} \quad (46)$$

$$\rightarrow C_2H_6 + C_2H_4 \quad (47)$$

$$C_2H_5^\cdot + I_2 \rightarrow C_2H_5I + I \quad (48)$$

$$C_2H_5^\cdot + C_2H_4 \rightarrow C_4H_9^\cdot \xrightarrow{C_2H_4} C_6H_{13}, \text{ etc.} \quad (49)$$

The absence of butane and higher molecular weight hydrocarbons among the photolysis products, whilst H_2 and C_2H_6 are present, means that the experimental results are incompatible with the above scheme. We cannot ascribe the formation of C_2H_6 to disproportionation of C_2H_5 radicals, because for thermal C_2H_5 radicals k_{47}/k_{46} = 0.1–0.2.

The absence of C_4H_{10} may be due to inhibition of the C_2H_5 radical by iodine. Also, according to Benson and others [77], the activation energy for the removal of hydrogen from HI by thermal alkyl radicals is 1–2 kcal mole^{-1}. Therefore, the formation of ethane (but not of butane) in the system may be explained by postulating the reaction

$$C_2H_5^\cdot + HI \rightarrow C_2H_6 + I. \quad (50)$$

However, if the C_2H_5 radicals are thermal, the difference between the effects of He and Ar inert moderators on the rate of formation of ethane is difficult to understand.

A kinetic analysis in which only thermal particles were considered also failed to agree with the experimental results.

The present writer has stated a hypothesis according to which hot $C_2H_5^*$ radicals are formed, during photolysis, by the combination of H* and C_2H_4, the reactivity of $C_2H_5^*$ being determined by the kinetic energy of the hot hydrogen atom:

$$H^* + C_2H_4 \rightarrow C_2H_5^*. \quad (51)$$

Hot $C_2H_5^*$ radicals with $E_{C_2H_5^*} = Q + E_{H^*}$ (where Q is the heat of addition of H to a C=C bond, 40 kcal mole^{-1}) can extract hydrogen from RH:

$$C_2H_5^* + RH \rightarrow C_2H_6 + R^\cdot \quad (52)$$

where RH = HI or C_2H_4, and reaction (52) proceeds either without activation energy (in the case of HI) or possibly with a small activation energy for extraction from hydrocarbons.

This hypothesis allows us to explain the experimental results. Thus, if the $C_2H_5^*$ radical is hot it will not be captured by iodine and will mainly give rise to C_2H_6 by reaction (52). If the radical is unable to react by (52) and becomes thermalised the resulting $C_2H_5^*$ is captured by iodine with formation of C_2H_5I. Additions of He lower $W_{C_2H_6}$ because H* rapidly loses energy by collisions with He (as a result of the comparable masses of H and He), and consequently the probability of reaction (51), and therefore also (52), decreases. Additions of Ar (Fig. 1) have no effect on $W_{C_2H_6}$ because the thermalisation of H* atoms is much slower on argon than on helium. This is confirmed by the negligible effect of Ar additions on W_{H_2}, showing once again that reactions (41) and (42) are "hot" reactions.

In order to explain the effect of composition on W_{H_2} and $W_{C_2H_6}$, the photolysis of HI–C_2H_4 mixtures was investigated over a wide range of concentrations of the two components. The experiments were made under steady state conditions at a constant pressure of HI (30 mmHg), so that the initial rate of formation of H atoms was constant. When photolysis is carried out in mixtures containing an excess of HI the main reaction of the H* atoms is (41), and only a small

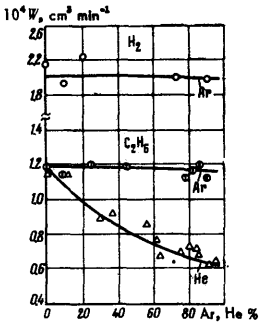


Fig. 1. Effect of He and Ar additions on W_{H_2} and $W_{C_2H_6}$ in the (C_2H_4 : HI = = 6 : 4)–Ar(He) system.

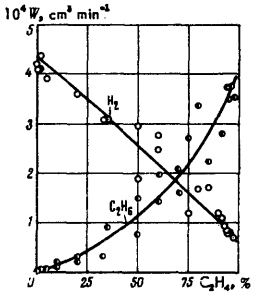


Fig. 2. Effect of composition on W_{H_2} and $W_{C_2H_6}$ in the HI–C_2H_4 system at 25° (P_{HI} = 30 mmHg).

fraction of the H* atoms will escape reaction (41) and take part in reactions (42) and (51). As the concentration of C_2H_4 in the mixture is increased, the contribution of reactions (42) [and particularly of reaction (51)] increases. The resulting $C_2H_5^*$ radicals can decompose, become thermalised, or take part in abstraction and addition reactions:

$$C_2H_5^* + HI \rightarrow C_2H_6 + I \quad (52a)$$

$$C_2H_5^* + C_2H_4 \rightarrow C_2H_6 + C_2H_3^* \quad (53)$$

$$C_2H_5^* + C_2H_4 \rightarrow C_4H_9^* \quad (54)$$

$$C_2H_5^* + M \rightarrow C_2H_5^* + M \quad (55)$$

$$C_2H_5^* \rightarrow H + C_2H_4 \quad (56)$$

Curves for the variation of W_{H_2} and $W_{C_2H_6}$ with composition are shown in Fig. 2. It can be seen that the decrease of W_{H_2} with increase of $[C_2H_4]$ is almost linear, whereas the increase of $W_{C_2H_6}$ shows a large departure from linearity.

It is important to note that the sum $W_{H_2} + W_{C_2H_6}$ is equal to the initial rate of formation of hydrogen in pure HI, to an accuracy of ±20%, over the whole concentration range. It follows that most of the H* atoms are consumed in reactions (41), (42), and (51), and that $C_2H_5^*$ radicals, unlike thermal $C_2H_5^*$ radicals, contribute mainly to the abstraction reactions (52) and (53) rather than to the addition reaction (54).

Introducing the condition

$$(W_{H_2})_0 \simeq (W_{H_2})_t + (W_{C_2H_6})_t \quad (VII)$$

and considering reactions (41)–(55), we can derive a kinetic equation of the form

$$\frac{W_{H_2}}{W_{C_2H_6}} = \frac{k_{42}}{k_{51}} + \frac{k_{41}}{k_{51}} \frac{[HI]}{[C_2H_4]}. \quad (VIII)$$

The plot of $W_{H_2}/W_{C_2H_6}$ against $[HI]/[C_2H_4]$ shown in Fig. 3 is evidently linear: from the intercept and slope of this straight line we can find k_{42}/k_{51} and k_{41}/k_{51}, and therefore also k_{42}/k_{41}. It turns out that $k_{42}/k_{41} \simeq 0.1$, in fair agreement with earlier results[22,28] for reactions of hydrogen abstraction from alkanes. Thus, the main reactions in the photolysis of HI–C_2H_4 mixtures are (41) or (51), according to whether HI or C_2H_4 is present in excess in the system. The ratio k_{53}/k_{52}, estimated by successive approximations, is also close to 0.1.

Hence, the principal reactions of hot H* atoms with E = 0.9–1.8 eV are those of extraction and addition at a π-bond, with formation of an excited radical. The excited $C_2H_5^*$ radical appears to be fairly long-lived, and is able to take part in chemical reaction (hydrogen abstraction) with RH until it decomposes.

The above estimates of k_{53}/k_{52} and k_{42}/k_{41} show that the cross-sections of these reactions depend to some extent on the strength of the bond, though the dependence is very much weaker (by several orders of magnitude) than in the case of thermal H atoms or $C_2H_5^*$ radicals.

It is important to note that the reactions of excited radicals are relatively insensitive to small additions of oxygen (Fig. 4), an efficient acceptor for thermal ethyl radicals.

Since the activation energy of reaction (50) is small (~ 1.5–2 kcal mole^{-1}), this reaction will compete with the "hot" reaction (52) only at elevated temperatures. Thus, it is interesting to examine the effect of temperature on $W_{C_2H_6}$ over a wide range of concentrations of HI–C_2H_4 mixtures. Fig. 5 shows temperature plots of $W_{C_2H_6}$ for 69, 90, 95, and 98% C_2H_4 respectively in the mixture. It is evident from the figure that even at 98% C_2H_4, when the hot reaction (41) can be effectively ignored, $W_{C_2H_6}$ is independent of temperature: this is evidence for the high efficiency of reaction (53). Helium additions cause the appearance of an activation energy (Figs. 5 and 6), the maximum value of E_{act} under full thermalisation of the hot H* atoms being ~ 1.5–2 kcal mole^{-1} (in agreement with the activation energy for the extraction of hydrogen from HI by thermal alkyl radicals). It must be noted that $W_{C_2H_6}$ decreases only by a factor of 2–3 at room temperature when H* atoms are fully slowed down. At lower temperatures (< 0°) the contribution of reaction (50) becomes less important, and $W_{C_2H_6}$ decreases more sharply.

It is interesting to consider the behaviour of excited radicals at low temperatures, when the thermal radicals are usually in a stabilised state. It has been reported[40,42] that CH_3^* could not be detected by ESR in the photolysis of CH_3I, although CH_4 was observed even at very low temperatures. When HI was photolysed in a matrix of 3-methylpentane[30] containing added alkenes (C_2H_4, etc.), ethyl, butyl, and other radicals were detected by ESR, though the authors consider that these were produced by the addition of thermalised hydrogen atoms to the alkenes. There are also data[32] on the photolysis of HI at 77°K in alkene matrices (C_2H_4, C_3H_6, see Table 2).

It is interesting to note that, as in our experiments on the gas-phase photolysis of HI–C_2H_4 mixtures, the main hydrocarbon product is C_2H_6 and the concentration of C_4H_{10} is low. Significant amounts of C_2H_5I are present: this

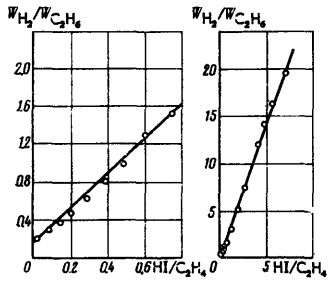


Fig. 3. Kinetic curve for Eqn. (VIII).

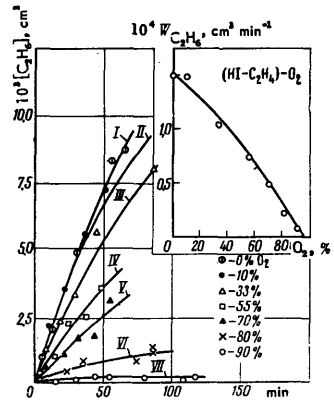


Fig. 4. Effect of added O_2 on the yield of C_2H_6 in the (C_2H_4 : HI = 6 : 4)–O_2 system: kinetics of the formation of C_2H_6 and $W_{C_2H_6}$ as a function of added O_2:
I) 0% O_2; *II*) 10% O_2; *III*) 33% O_2; *IV*) 55% O_2; *V*) 70% O_2; *VI*) 80% O_2; *VII*) 90% O_2.

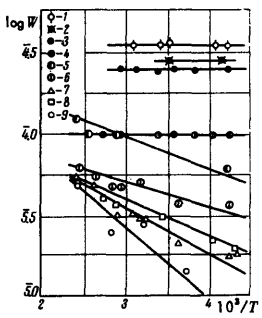


Fig. 5. Effect of temperature on $W_{C_2H_6}$ in the photolysis of HI–C_2H_4 and (HI–C_2H_4)–He mixtures:
1) HI : C_2H_4 = 2 : 98; 2) HI : C_2H_4 = 5 : 95; 3) HI : C_2H_4 = 1 : 9; 4) HI : C_2H_4 = 4 : 6; 5) (HI : C_2H_4 = 1 : 9) + 85% He; 6) (HI : C_2H_4 = 4 : 6) + 50% He; 7) (HI : C_2H_4 = 4 : 6) + 85% He; 8) (HI : C_2H_4 = 4 : 6) + 92% He; 9) (HI : C_2H_4 = 4 : 6) + 98% He.

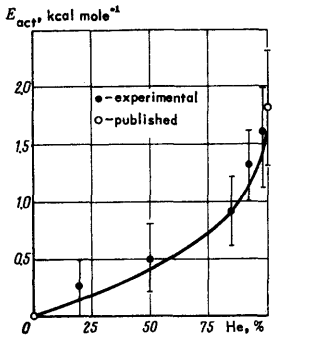


Fig. 6. Variation of the activation energy for hydrogen abstraction by ethyl radicals with concentration of added helium in the photolysis of the ternary mixture (HI : C_2H_4 = = 4 : 6)–He. The open circles are E_{act} data for hydrogen extraction from HI by thermal alkyl radicals.[77]

TABLE 2. Photolysis of HI–C_2H_4 and HI–C_3H_6 mixtures at 77°K (after Hughes and Purnell[32]).

Matrix	Irradiation time, min	Photolysis products	Amount, mol. %
HI 150 μmole C_2H_4 15 μ mole	65	C_2H_6	29
		n-C_4H_{10}	1
		C_2H_5I	70
		C_2H_2, C_4H_9I, C_4H_6, C_6H_{14}, C_3H_3I, C_1- and C_3-iodides	<1
HI 125 μmole C_3H_6 25 μ mole	40	C_3H_8	28
		2,3-dimethylbutane	2
		n-C_3H_7I	3
		i-C_3H_7I	67
		allene, diallyl, cyclopropane, C_3H_5I, methylacetylene	traces

may be ascribed to capture of ethyl radicals by I_2. The authors have put forward a hypothesis involving the formation of a reactive complex in the matrix when a photon is absorbed, followed by reactions within a cell. However, their results can be interpreted in terms of the formation of "hot" C_2H_5 radicals, produced by reaction (51), which are highly reactive even at liquid nitrogen temperature and can therefore abstract hydrogen from RH.

The results discussed above demonstrate that hot H* atoms with 1–3 eV energies have some special features as compared with thermal hydrogen atoms and very fast atoms (such as tritium recoil atoms): in particular, a weak temperature dependence of the rate of the abstraction reaction is possible near the chemical reaction threshold. When the energy is increased in the range 1–3 eV and above, the reactivity of the H* atoms increases. Studies of the reactivity of hot H* atoms in the energy range of a few electron-volts are particularly important, because these atoms can be formed in many photolytic reactions and during radiolysis. In particular, by reacting with alkenes these atoms can produce excited radicals as reactive intermediates which influence the final product distribution.

The formation of hot $C_2H_5^*$ radicals in the radiolysis of C_2H_4 and NH_3 was demonstrated by the present writer[17].

Hot H* atoms are formed by the radiolytic decomposition of excited RH molecules:

$$RH^* \rightarrow R^{\cdot} + H^* \qquad (57)$$

where RH = C_2H_4, NH_3, etc.

The ratio $C_2H_6 : C_4H_{10}$ serves as a measure of the energy of the $C_2H_5^*$ radicals. This ratio is appreciably higher than 0.1–0.2 (the value of k_{disp}/k_{rec} for thermal C_2H_5 radicals), and can approach unity [17,75,78-81] in the radiolysis of C_2H_4 and exceed unity in the radiolysis of C_2H_4–NH_3 mixtures [17,75]. The ratio is not a function of the pressure in the system or of temperature (in the range from +50° to -78°), and decreases when He is added to C_2H_4 or to a C_2H_4–NH_3 mixture [17,75]. Thus, as in the photolysis of HI–C_2H_4 mixtures, the enhanced yield of C_2H_6 in the radiolysis of pure ethylene and of ethylene mixed with RH can be explained starting from the hypothesis that a reactive intermediate (the excited ethyl radical) is formed. It is significant that in the radiolysis of NH_3–C_2H_4 mixtures small additions of O_2 affect the yield of C_4H_{10} (Fig. 7) more strongly than that of C_2H_6: this is difficult to understand on the assumption that these products are formed exclusively by reactions (46) and (47). An interesting observation made on the radiolysis of C_2H_4 at -196° is that not only did the $C_2H_6 : C_4H_{10}$ ratio not fall off, but it was even greater than unity, showing that the reactive $C_2H_5^*$ radical can be formed even at low temperatures [80].

The formation of reactive $C_2H_5^*$ radicals is obviously not specific to ethylene. The features obtained should be observable, to a greater or lesser extent, in the addition to alkenes of hot hydrogen atoms obtained both by the decomposition of excited molecules in radiolytic and photolytic processes and in chemical reactions accompanying nuclear transformations.

In contrast to the excited radicals obtained by the decomposition of a molecule, we have the new concept of an excited $C_2H_5^*$ radical formed by the collision of an ethylene molecule with a fast hydrogen atom. Whether under these conditions a vibrationally excited radical is formed, or whether electronic excitation can occur, is still not fully clear, because the electronic levels of $C_2H_5^*$ are not known.

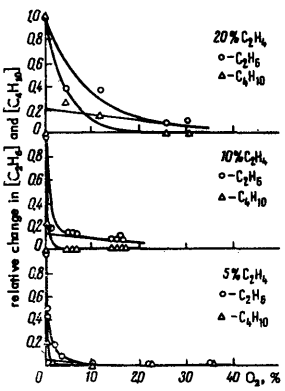


Fig. 7. Effect of added O_2 on the relative change in the yield of C_2H_6 and C_4H_{10} during radiolysis of (NH_3–C_2H_4)–O_2 mixtures. (Dose rate 1.2×10^{14} eV cm^{-3} s^{-1}, irradiation time 40 h.)

We know that the C_2H_4 molecule has low-lying electronic levels: 1.7, 4.4, 7.7, and 9.2 eV. [82] Since the levels of the $C_2H_5^*$ radical must lie below those of the $C_2H_4^*$ molecule, we cannot exclude the possibility of excitation of the electronic levels of $C_2H_5^*$ ($E_{C_2H_5^*} \simeq Q + E_{(H^*)} \simeq 3.8$ eV). When discussing kinetic mechanisms it is essential to make allowance for the possible formation of excited particles having enhanced reactivity. This is specially important in the case of photochemical processes occurring in the vacuum ultraviolet region (λ = 1236, 1440 Å) and during radiolysis, when hot atoms and radicals having several electron-volts of excess energy can be formed. "Hot" intermediate products (molecules, atoms, radicals) can be expected to form also in the reactions of recoil atoms, particularly tritium, with alkanes [2,9] as well as with alkenes [10].

Studies of the reactions of hot atoms and radicals having energies of the order of a few electron-volts should help to fill a gap in one of the most interesting regions of chemical kinetics: the region of intermediate energies, comparable with the energy of the chemical bond, which (unlike the high energy and the thermal energy regions) is as yet inadequately investigated.

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QUARTZ CERAMICS

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I. INTRODUCTION

Quartz ceramics are a recently developed class of materials offering a range of valuable properties of particular interest in a number of new technological areas.

Modern technology often requires materials combining high dimensional stability over a range of temperatures with good thermal stability and low thermal conductivity.

Fused quartz has a very low coefficient of thermal expansion: it is used as a standard for assessing the relative temperature stability of materials and has been successfully incorporated in equipment for use at high temperatures [1-9]. However, because of the very high viscosity of molten quartz glass (exceeding that of ordinary glass compositions [10] by more than a factor of 100 at 2000°), and of its appreciable volatility, the fabrication of articles of quartz glass presents serious difficulties.

Furthermore, only a very limited range of sizes and configurations can be obtained by applying conventional glass technology to the production of quartz glass articles. Hence, we must look for alternative routes to the production of articles made from fused quartz.

The limitations in shape and size are being overcome by the success achieved in recent years in applying ceramic technology to the problem.

It should be noted that an established terminology for ceramic materials based on amorphous or crystalline silica is still lacking, and some clarification is essential. In the American literature we find the term "slip cast fused silica", in the German Democratic Republic "Quarzglaskeramik" (quartz glass ceramic) and "schlickergegossenes Quarzgut" (translucent quartz glass made by slip-casting). In the USSR, the terms "kvartsevaya steklokeramika" [3] (quartz glass ceramic) and "kremnezemnaya steklokeramika" [11] (silica glass ceramic) have been proposed for materials based on quartz glass (fused quartz), and "kersil" for a ceramic based on synthetic amorphous silicon dioxide [12].

We consider the term "steklokeramika" (glass ceramic) an unfortunate choice, because it implies a crystallised glass of the "Pyroceram" type. Our suggested term "kvartsevaya keramika" [13] (quartz ceramic) can be applied to all ceramic materials prepared by ceramic techniques from one of the following: fused quartz, synthetic amorphous silica, or crystalline silica. It is important also to distinguish between the various forms of raw material used for the ceramic (crystalline silica, quartz glass, silicic acid gel), because the type of raw material plays an important role in the technology and in determining the properties of the product.

Several methods of preparation of quartz ceramics are known. The first, proposed by Skaupy and Weissenberg [14,15], consists in fusing (at 1650–1680°) cold-formed articles of quartz sand.

The second method, proposed by Solomin [11], consists in preparing articles of finely powdered quartz glass by the slip-casting method, with a subsequent heat treatment.

The difference between these methods lies in the choice of starting material. In the former, the starting material is quartz sand or rock crystal, which is converted to the desired state in the finished article. This requires a much higher temperature than is used in the second method. In the latter method the starting material is finely divided fused quartz. However, the basic technological operations needed to prepare the ceramic from fused quartz and from crystalline silica are identical. The fields of application of the second method and the quality of the articles made from fused quartz are such that this method is emphatically the better.

Botvinkin and Zaporozhskii [3] have described a method of preparation of quartz ceramics devised in an attempt to develop a material with a higher thermal stability than ordinary quartz glass. Aqueous silica gel was used as a binder for the fine grains of a thermally stable glassy composition, thus duplicating the natural conditions for the formation of cementoquartzites, whose thermal stability is equal to that of optical quartz glass.

It was shown [3] that the high thermal stability is due to the specific properties of the solid silica gel which binds the crystalline grains of natural quartz, itself of indifferent thermal stability. A series of materials with a binder of the silica gel type was synthesised, in which finely divided, transparent or translucent quartz glass was the filler.

Heany [16] suggested a method for preparing articles from finely disperse silica obtained by the decomposition of various silicone compounds. The castings were fired at 1200–1500° for various times.

The many papers published in the last few years [17-53] have considerably extended the scope and the applications of this new material, have suggested a number of valuable improvements in the technology of its production, and have discussed some of its properties.

II. MATERIAL PREPARATION

The starting material for the preparation of ceramics from quartz glass consists of waste, transparent or translucent, quartz glass [23,30], or fused quartz with SiO_2 content of the order of 99.5% (as reported by Schulle [23]). The quartz glass should be carefully melted and free from coarse heterogeneous inclusions such as graphite, slag, etc. In the preparation of the ceramic from silica, the starting material is pure silica sand or rock crystal. Schulle and Ulbricht [24] find that quartz sand with SiO_2 content of not less than 99.6% is essential for high-quality articles. By studying separate fractions they showed that the impurities in the sand are concentrated in the fractions of less than 0.1 mm and more than 0.3 mm grain size: the 0.1–0.3 mm fraction, which accounts for over 90% of the quartz sand, was therefore used for preparing articles.

In order to increase the SiO_2 content, the sand was treated with 12% hydrochloric acid in a ball mill for one hour. The chemical composition of the milled and washed quartz sand and glass, and the size distribution of quartz glass [23,24], are given in Table 1.

TABLE 1. Chemical composition of quartz sand and quartz glass, and granulometric composition of quartz glass.

	Quartz sand, wt. %	Quartz glass, wt. %	Size of fractions, μm	Fractions, %
SiO_2	99.83	99.51	40	0
Al_2O_3	0.07	0.31	22—40	15.1
Fe_2O_3	0.01	0.03	10—20	8.6
CaO	0.03	0.06	5—10	12.3
MgO	0.01	0.04	2—5	24.6
$K_2O + Na_2O$	0.01	0.05	2	39.4

Impurities of alkali metal oxides are the most detrimental, because they induce and catalyse the cristobalite transformation.

Amorphous synthetic silica also may be used as a raw material for the preparation of quartz ceramics. The first technological operation in this case is to bake the raw silica in order to drive off the large amounts of adsorbed water. It has been reported[3] that as much as 70–100 g of water per 1 kg of charge can be removed from synthetic silica in 24–72 h by baking at 1000–1200°.

Certain impurities are frequently added to the charge in order to improve sintering and inhibit crystallisation. In this case the SiO_2 content becomes correspondingly lower.

For example, Palatskii[51] mentions the addition of kaolin and low-melting glass frit, which lowers the sintering temperature to 1050–1100°. A slight lowering (by 20–30°) of the sintering temperature of a ceramic made from fused quartz can be achieved by adding synthetic SiO_2, whose sintering and crystallisation temperatures are both lower. Other workers[37] have added B_2O_3 to inhibit crystallisation.

Quartz ceramics based on quartz glass have undergone by far the most intensive development in recent years: all the results quoted in this review will therefore apply to this type of ceramic unless accompanied by a statement to the contrary.

Quartz glass is comminuted in a jawbreaker or other type of crusher; still finer particles are obtained in a ball mill. Size analysis of the fine powder is carried out in a centrifugal air separator[49].

Fine milling is done in ball mills with quartz liners and quartz balls; vibratory mills also can be used[35]. In cases of iron pick-up magnetic separation must be resorted to[49,50]. The fineness of the powder can be controlled on a PSKh-2 apparatus[35]: fine powders with a specific surface area as large as 8000–10 000 $cm^2 g^{-1}$ have been prepared both for semi-dry pressing and for slip casting[35].

III. FORMING

Quartz ceramics are manufactured in various forms: with medium porosity (up to 20–30%), high porosity (up to 80%), foamed quartz ceramic[34,39-42,44], and ceramic from cast[20,32] or granular material[35]. The following methods of forming quartz ceramic are known: wet slip casting, semi-dry pressing, hot pressing in graphite moulds, hot casting from wax, extrusion, etc.

The slip casting method is the most widely used, probably because of the requirement for hollow articles, which are most conveniently formed by this method.

The slip consists of a concentrated suspension of very fine particles of SiO_2 in a dispersion medium (water).

The particles must be fine enough to prevent fast settling under the influence of gravity during the time needed for the casting process. From the difference in density between the solid and the liquid phase and a number of other factors it can be calculated[54] that the particle size should be in the range 0–10 μm. The size of the bulk of the particles should be such that the interactions between particles are determined essentially by surface forces rather than by gravity.

The dispersity of the material is characterised by the particle size distribution, which is measured by sedimentation analysis, but as an overall characteristic of the dispersity we can use the computed mean surface diameter given by the formula

$$d_{mean} = \frac{100}{\sum \frac{a_i}{d_i}},$$

where a_i is the proportion of each fraction in % and d_i is the nominal mean diameter of the respective fraction in μm.

A very important process takes place during milling of quartz materials: formation of silica gel, as a result of which the non-plastic material acquires some measure of plasticity. Gel formation results from the disruption of the crystal lattice at the surface of the quartz particles during milling, accompanied by chemical reaction between water and the SiO_2.[55,56] When the grain size is less than 0.5 μm the disturbance of the crystal lattice can extend throughout the bulk of the particle, as shown by differential thermal analysis curves[24].

All types of silica (quartz, cristobalite, vitreous silica) can be considered as SiO_2 aggregates[57]. If the exact stoichiometry SiO_2 is retained, a truncated tetrahedron must be present at the point of contact of tangential surfaces. A surface of silicon atoms tends to complete its tetrahedral coordination: at a water interface the coordination can be completed by the formation of OH groups at the surface of SiO_2. Hydration of the silica proceeds at the surface and is limited by the size of the particle.

It is possible to obtain a silica slip (by wet milling) without any binder or plasticiser additives. The slip is prepared (by "wet" milling) in ball mills with silicon or quartz balls and a quartz liner. Rubber-lined mills with silica balls can also be used. The use of other types of mill is not recommended if pick-up of harmful impurities is to be avoided. The slip is made up of distilled water and quartz powder ground in the mill until the required consistency and the prescribed particle size distribution are obtained. The milling time can vary over wide limits (20–100 h), depending on the size distribution of the starting quartz, on the amount of water present, and on many other factors. Nishanova and coworkers[35] prepared a slip of satisfactory quality by milling for 30 h a powder of 10 000 $cm^2 g^{-1}$ specific surface area. The water content of the slip is between 25 and 30%: at higher moisture levels shrinkage increases and the quality of the castings deteriorates.

When the impurity content of the starting material increases, the minimum permissible water content rises to 33–35% or higher. Since a decrease in the water content of the slip can have an effect on the subsequent production stages, attempts have been made[35] to minimise the wetness of the slip by using vibration during casting (vibro-casting). The slip used in this work had a water content of 20%. The optimum time of vibration of the moulds (50 Hz frequency, 1 mm amplitude) was 3 min.

The degree of milling of the slip must be such that 40–50% of the solid particles have a diameter less than 5 μm. If the solid phase in the slip has a coarser size, fast settling results, giving poor casting properties and castings of low mechanical strength. The correct size distribution of particles is also essential. Preponderance of one fraction leads to increased shrinkage, lower strength, and lower density, which hampers the subsequent sintering.

The viscosity of the slip is very important in slip casting. The most satisfactory method of measuring viscosity under these conditions is to time the delivery of 100 cm^3 of the slip from a pipette (Engler's apparatus). It has been shown that the optimum pH value for a slip containing crystalline SiO_2 is 1; this value was obtained by adding hydrochloric acid, which does not introduce undesirable impurities into the slip[24].

The present writers have found[45] that the minimum viscosity of a slip based on fused quartz is reached at pH 3–3.5. Addition of hydrochloric acid lowers, however, the strength of the castings. For example, when the pH was lowered from 5.9 to 1.6 the strength of the castings under bending decreased from 4.0 to 1.4 kg cm^{-2}. This can obviously be ascribed to decomposition of the silica gel formed during the wet milling process, which acts as a binder in this case.

However, the pH changes continuously during wet milling due to the formation of silicic acid, reaching pH 3.5–5 at the completion of milling from an initial value of 7. Thus, the optimum pH value is obtained without adding acid.

The slip casting method is used for manufacturing hollow articles; the mould material is plaster of Paris, and the passive part of the mould is made of aluminium, plastics, etc. Ceramic or paper moulds can also be used[18,38].

The high thixotropy of SiO_2 slips is noteworthy. The limiting to apparent viscosity of thixotropy varies between 2 and 3, and increases steeply with particle size.

Using a thixotropic slip, articles cast in wooden moulds have shown adequate strength. The moulds were then dismantled and the articles dried[32].

The most important criterion of the quality of slip casting is the density of the casting obtained. This is because a high density is very beneficial to the relatively low mechanical strength of the dried castings, and it minimises shrinkage during drying and firing (particularly important in the manufacture of items of large dimensions and complex shape). Sintering also is easier and faster with high-density castings. The density depends on the particle size of the solid phase present in the slip, and on the size distribution over the various fractions, because separate loose aggregates of particles lower the density of the casting. Equally important is complete removal of air bubbles from the slip, which can be achieved by vacuum treatment. Under otherwise identical conditions, the density and the mechanical strength of the dried slip vary almost linearly with grain size (Fig. 1).

One of the features of ceramics manufactured from fused quartz is the possibility of obtaining castings of low porosity and high mechanical strength as compared with other types of ceramic.

The present writers have shown[45] that the casting properties of the slip are improved by lengthy storage after milling. Depending on the characteristics of the slip, the optimum properties were developed after 3–7 days: the

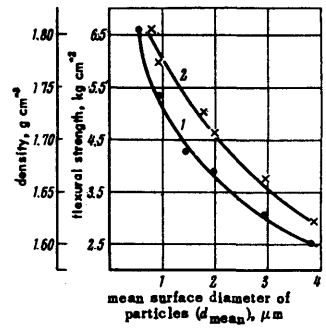


Fig. 1. Variation of density (1) and of flexural strength (2) of dry specimens with mean surface diameter of the particles (d_{mean}).

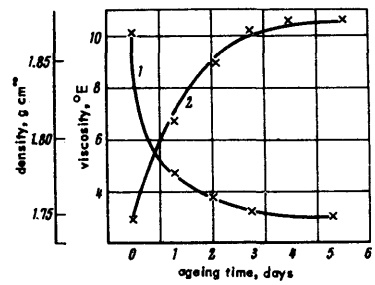


Fig. 2. Effect of ageing time on the properties of the slip and of the castings:
1) viscosity of the slip; 2) density of the castings.

viscosity decreased 2–8-fold, and the viscosity ratio changed from 2–3 to 1.2–1.3. Castings made from this slip can have a porosity of less than 12% and a strength of 25 kg cm^{-2} in transverse bending (Fig. 2).

We interpret the favourable effect of storage as follows. The silica gels formed during the wet milling process age with time; this is accompanied by evolution of the dispersion medium (water) from the diffusely bound to the free state, and therefore also by a decrease in viscosity. During the setting process closer packing can take place, because the diffusion layer around the particles is thinner.

Both the overflow and the pouring methods of casting can be used for the manufacture of quartz ceramics. Radome castings 750 mm in height and 450 mm in diameter have been made by the former method, which lends itself to the production of large articles without difficulty[18]. A radome 1220 mm in height also has been made by slip casting[36].

A mould release agent is used to prevent adhesion of the articles to the mould: for example, sodium alginate, which allows the passage of water[18]. However, the sodium alginate must be removed from the surface of the articles before baking, because it can cause undesirable crystallisation if it is allowed to penetrate into the material. In most cases, even a small shrinkage of the casting in the mould is sufficient to free the object without using release agents.

It is worth stressing that the shrinkage during drying is very small (0.1–0.5%, depending on the particle size and on the water content): hence, the size of articles which can be made by slip casting[18] can reach several metres, corresponding to a weight of 500 kg.

Quartz ceramics are also formed by using the slip casting method with 3–10% additions of a water-soluble gum. The article is dried, and the gum is hardened at 150–200°, which raises the strength of the unbaked articles in bending to 500 kg cm^{-2}. The gum burns off during sintering, but there is a loss of mechanical strength proportional to the amount of resin binder. Impregnation is used to achieve greater strength. The main advantage of this method of forming is that it allows the article to be machined on a lathe before baking. In this way one can make components with machine-cut screw-threads, electrical insulators of any shape, and nose cones for guided missiles[23].

A modification of slip casting is casting from compositions with a granular filler (casting compositions); another modification is casting from foaming slip. Casting from casting compositions consists essentially in adding to the normal slip a filler of granular fused quartz[31,35] of particle size between 0.25 and 1 mm.

To make larger castings, the maximum fraction size is increased. Under these conditions the ratio of slip to granular filler is of the order of 1 : 1. It is recommended that 100 parts by weight of the filler should be triturated with 2 parts by weight of water immediately before mixing with the slip. By using vibration during casting it is possible to lower the water content of the slip to 14.5–17.5%.[35]

Drying quartz ceramic presents no difficulty because the shrinkage is very small (less than 1%), and there are no distortion or crack formation problems. Both spontaneous drying at room temperature and forced drying in drying chambers can be used. A combination of the two methods is most common: 24 h at room temperature followed by treatment at 120° in a special drier[18]. The drying time is determined by the wall thickness of the article. For 10–15 mm wall thicknesses, drying is practically complete in 3–4 days at room temperature.

We may expect, however, complications to arise in the drying process as a result of the strong tendency of the slip towards gel formation when the particle size is made very small or the milling time is increased. This is because silicic acid gel does not readily give up OH groups on drying. In this case the drying procedure must be milder, and must be chosen to suit the fineness of milling, the degree of gel formation, and the size of the casting.

Foamed quartz ceramics are becoming very common: they are produced by slip casting with a suitable foaming agent in the slip.

Budnikov and Duderov have developed a new method for preparing highly porous articles on the basis of fused quartz[34]. The fused quartz, finely divided to an average particle size of 1–3 μm, is mixed with acid aluminium phosphate and with glyceryl adipate, and the foaming agent "Product 102-T" (methylphenylene di-isocyanate) is added to the resulting suspension. The starting mass has the following composition (in wt.%):

fused quartz	45.0
ester	20.9
foaming agent	13.2
aluminium phosphate	20.9

A mass of the above composition is foamed in closed steel moulds, allowing accurate control over the profile of the article. Foaming occurs as a result of the evolution of carbon dioxide by the reaction

$$n\mathrm{O{=}C{=}NRN{=}CO} + n\mathrm{HOOCR'COOH} \rightarrow n\mathrm{CO_2} + n\mathrm{O{=}C{=}NRNH{-}C(=O){-}R'{-}C(=O){-}OH}.$$

di-isocyanate (foaming agent); ester

The volume expansion obtained is greater than a factor of 10. The polymerisation of the polyester, which occurs at the same time as the evolution of carbon dioxide, strengthens the porous structure and gives it increased rigidity. Firing temperature 950–1000°, density of the finished article 0.33–0.40 g cm^{-3}, proportion of open pores 80–88%.

According to Walton, aluminium phosphate (which was examined as a possible impregnating material) induced cristobalite transition of the siliceous masses[33]. However, X-ray diffraction analysis of the specimens fired at 1000° for 28 h, and also at 1100°, did not reveal a more intense peak than the one formed during normal heat treatment and ascribed to cristobalite (Fig. 3). Hence it was suggested that the observed peaks are associated not with cristobalite (as assumed by Walton) but with cristalorphite, the cristobalite form of $AlPO_4$. The absence of cristobalite was later confirmed by differential thermal analysis, petrographic analysis, and dilatometric analysis.

According to an American patent[45], insulators are made from silicic acid and glycerol (1–5%): after mixing, the mass is dried at 120–300°, ground to 100 μm particle size, and furnaced at 1260–1650°, when the silica expands forming hollow microspheres. The density of the final product is 0.7–1.2 g cm^{-3}.

Hot casting from wax can be used as a casting method. The density of the articles in this case is lower than when slip casting is used. Articles of simple shape can be made by semi-dry pressing, using a specific pressure of between 800 and 1200 kg cm^{-2}. The water content of the powder lies between 8 and 10%. The granular composition is approximately the same as in slip casting. According to Nishanova and coworkers[35] the specific gravity of the pressings and their apparent porosity vary with the pressure used as shown in Fig. 4. The relatively high porosity of the semifinished product is worth noting, as it causes difficulties in the subsequent sintering. Owing to the low mechanical strength, reaching 4–6 kg cm^{-2} in bending after forming and 2–3 kg cm^{-2} after drying[24], additives are commonly used.

Ethyl silicate-40, an ester of silicic acid, has been found[23,24] to be a very effective additive. Under the influence of water this compound hydrolyses to give SiO_2 gel, and binds the quartz particles together. The binding effect persists at elevated temperatures, which makes this binder superior to dextrin, starch, etc.

Ethyl silicate-40 decomposes to amorphous silica which is transformed to cristobalite only after prolonged heating at temperatures in excess of 1000°. Furthermore, ethyl silicate-40 does not increase the tendency to crystallisation of a quartz ceramic, and does not introduce contamination.

Alternatively, 0.2% additions of urea–formaldehyde resin have been used[35].

Vasilos and Wagner[27] have described a method of preparation of quartz ceramics from ground quartz glass by hot pressing in graphite moulds, which involves the simultaneous application of heat and pressure. Hot pressing

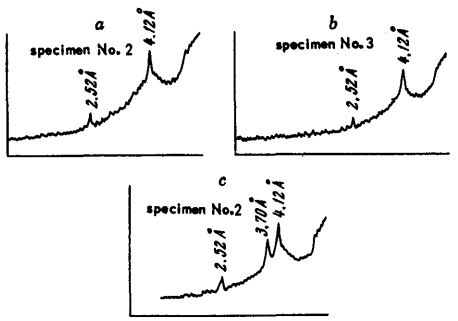


Fig. 3. X-Ray diffraction patterns of specimens: (*a*) fired at 1000°; (*b*) fired at 1100°; (*c*) fired at 1000° for 28 h.

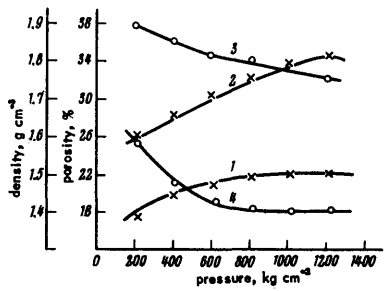


Fig. 4. Variation of the apparent porosity and of the density of a quartz ceramic with the porosity and the density of the raw material and with the applied pressure:
1) density before firing; 2) density after firing;
3) porosity before firing; 4) porosity after firing.

was achieved by applying pressure for 3 h at 1050–1450°. Graphite, which burns at ~800°, is added to the powdered quartz glass. Sintering under pressure results in relatively large shrinkage, which can amount to 5–15% or more according to the compressive strain. The porosity of the resulting material is less than 3%. If necessary, quartz glass articles with regions of different porosity can be manufactured by this method.

Vasilos[26] used three arbitrarily chosen fractions of fused quartz in the range 5–300 μm, prepared by grinding followed by acid leaching and separation on sieves.

Studies carried out on the hot pressing apparatus have shown that at 1100°, 1150°, and 1200°, and pressures in the range 70–170 kg cm^{-2}, for pressing times up to 90 min, the dispersity of the fused quartz has a negligible effect except for fractions up to 300 μm in size.

IV. THE ONE-COMPONENT SYSTEM AND ALLOTROPIC TRANSFORMATIONS OF SiO_2

The existence of the following modifications of silica is now recognised: quartz, tridymite, cristobalite, coesite, kitite, fibrous silica, stishovite, and quartz glass.

Fenner's well known phase diagram for SiO_2 clearly shows all the most important states of silicic acid (quartz, tridymite, cristobalite). It does not, of course, include all the recently discovered modifications listed above: for a detailed discussion of these allotropes and of contemporary ideas on silicon dioxide the reader is referred to the original papers[58–64].

Fenner's diagram shows the variation with temperature of the vapour pressure of the various modifications of SiO_2: polymorphic transformations are presented graphically.

Second-order transitions (within a given modification) are fast, but first-order transitions of the quartz–cristobalite type are slow. Hence, the temperature limits of stability of the individual modifications are meaningful only for prolonged heating in the presence of strong mineralisers. The smaller the difference in structure of the crystal lattices of two polymorphic forms of SiO_2, the faster is the transformation (under otherwise identical conditions).

In Fenner's diagram quartz is shown as thermodynamically stable from low temperatures up to 870°, tridymite from 870° to 1470°, and cristobalite from 1470° to the melting point.

The following problems are important in a study of the technology, structure, and properties of quartz ceramics: (1) the transformation of pure (upwards of 99% SiO_2) silica, quartz glass, and amorphous synthetic SiO_2 at the heat treatment temperatures into cristobalite, and the kinetics of this transformation; (2) the transition from high-temperature to low-temperature cristobalite; (3) the influence of impurities, of the gas medium, and of various other factors on these transformations.

Fenner's phase diagram for silica was not re-examined for many years. More recently it has been repeatedly pointed out that quartz is not converted into tridymite in the absence of mineralisers, and that Fenner obtained tridymite by using Na_2WO_4 as a mineraliser[65–69]: revision of the diagram therefore seemed desirable[70]. It was subsequently shown that pure silicon dioxide under atmospheric pressure can be converted into quartz or cristobalite by heating[71,72].

Flörke electrolysed crystalline samples of tridymite[73] in the temperature range 870–1470°. Under these conditions, the tridymite in the anodic region was converted into cristobalite (for electrolysis temperatures above 1000°) or into quartz (at temperatures below 1000°), suggesting the breakdown of the tridymite structure by the removal of a stabiliser.

Thus, the stability of tridymite is due to impurity atoms of alkali metals introduced into the lattice during the synthesis of tridymite.

The structure of tridymite, like that of other modifications of silica, consists of a particular sequence of layers of SiO_4 tetrahedra. When free from defects, tridymite should have a twofold periodicity of layers of SiO_4 tetrahedra, i.e. an AB|AB|AB|AB structure.

Like cristobalite, real crystals of tridymite contain regions showing twofold periodicity and others showing threefold periodicity. However, in contrast to cristobalite which is made up mostly of three-layer regions, two-layer regions are predominant in tridymite.

According to Flörke, tridymite should be treated as a highly defective form of cristobalite, and should not appear in the phase diagram. Flörke's revised phase diagram, shown in Fig. 5, includes only quartz and cristobalite, with a transition temperature in the region of 1050°: pure cristobalite does not change into any other crystalline form[74,75].

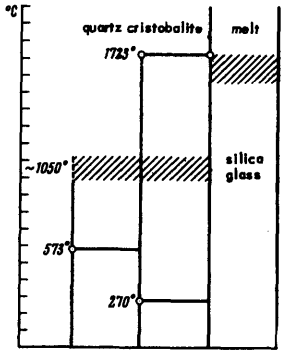


Fig. 5. Tentative revision of the phase diagram of pure SiO_2 (after Flörke).

Thus, whether we start from pure quartz, pure cristobalite, or from an amorphous form of silica (such as quartz glass or dehydrated silica gel), tridymite is not formed even after lengthy treatment in the temperature region 870–1470° (the stability region of tridymite according to Fenner). However, in the presence of small quantities of alkali metal oxides, tridymite forms quite readily in the stated temperature region. It follows that two phase diagrams for silica are needed, depending on the experimental conditions. When very pure silica is used (by far the commonest case in the preparation of quartz ceramics) the transformations are dictated by Flörke's diagram, but if the silica is in contact with other substances (in particular with alkali metal salts) Fenner's diagram should be used[58].

During the last few years many papers have been published on the allotropic transitions of SiO_2 and on the kinetics of crystallisation, and on the influence of various factors on these processes[82-110].

V. CONVERSION TO CRISTOBALITE AND ITS KINETICS

It has often been observed that the transformation of quartz to cristobalite, a solid-state reaction[95], begins at the free surfaces of grains, both internal and external. under the influence of high temperatures the cristobalite transformation of quartz spreads from these surfaces. The transformation of quartz follows this course because the free surface is the site of broken bonds between $[SiO_4]$ tetrahedra, which facilitate the rearrangement of the lattice through the enhanced mobility of the tetrahedra. The accurate and constant correlation between the crystallographic directions of quartz and of the resulting cristobalite is evidence that this transformation occurs in the solid phase.

By treating quartz glass as a non-stoichiometric material with a definite proportion of oxygen defects, Boganov and coworkers[104] explain the formation of a crystalline layer on the glass surface as follows.

When the surface of the glass is exposed, at high temperatures, to an oxygen-containing atmosphere, oxygen atoms penetrate the glass network by thermal diffusion. During some induction period, a fraction of the oxygen atoms dissolved in the boundary layer of glass fills, at random, vacant anion sites to an increasing depth below the original surface. However, formation of a local crystalline block in the region which has been made stoichiometric is possible only when this region reaches a definite critical size. This size is determined by the conditions of equilibrium between the deformation forces associated with the excess energy of a stoichiometric but disordered region and the bond-breaking forces at the surface of the resulting crystalline block. If the supply of the required amount of oxygen to the subsequently formed blocks is fast as compared to the characteristic formation time of the block the crystallisation process should proceed at a constant rate.

The temperature at which the cristobalite transition occurs during firing of a quartz ceramic is of the utmost importance, because the forms of quartz most resistant to the transformation (quartz glass) offer the best prospects of dense sintering and therefore also of improvements in a number of properties. The high-temperature α-cristobalite formed during heat treatment goes over to the low-temperature β-cristobalite during cooling: the attendant decrease in volume loosens the structure of the ceramic and degrades its thermal stability.

A more detailed study of the cristobalite transition temperature and of its dependence on a number of factors is therefore essential. The cristobalite transition temperature (1050°) given in Flörke's diagram is not associated with any particular heating time or with various other factors often found to be critical. According to Walton[31-33] and others, a fused quartz ceramic converts to cristobalite at temperatures above 1093° (2000°F). According to Schulle[23], conversion to cristobalite at 1100° occurs only after upwards of 20 h heating.

Verduch[82] studied the effect of time and temperature on the rate of formation of cristobalite, and showed that three stages are involved in cristobalite formation: the formation of crystal nuclei, fast crystallisation, and the subsequent (slow) crystallisation. The amorphous SiO_2 used for the investigation (silicic acid) began to crystallise at a temperature as low as 945° after 41 h, and at 985° crystallisation set in after 10 h.

The temperature variation of the nucleation process is described by the equation

$$\log t = \frac{22462}{T} - 13.32,$$

where t is the time needed for the formation of nuclei in seconds and T is the absolute temperature in degrees.

When the temperature is raised from 945° to 1085° the nucleation time decreases from 41 h to 0.5 h.

The next stage is the growth of a cristobalite structure. The amount of cristobalite formed is given by the equation

$$\log K = 5.98 - \frac{11122}{T},$$

where K is the amount of cristobalite formed per second (%), and T is the absolute temperature in degrees.

On raising the temperature from 945° to 1085° the quantity K increases from 7.87×10^{-4} to 7.00×10^{-3}.

The temperature at which cristobalite is crystallised from silicic acid determines the interplanar spacing of the cristobalite lattice, which decreases from 4.0825 Å to 4.062 Å when the temperature is raised from 1080° to 1425° (corresponding to a perfect cristobalite structure at 1425°).

The ordering of the structure proceeds from the centre of the crystal towards the periphery. The kinetics of the conversion of pure quartz into cristobalite depend on the

crystallite size. When the grains are small (~50 μm) the transformation in the temperature region 1270–1450° follows the equation

$$\log\alpha = -\frac{3ut}{r},$$

where u is a constant, t is the heating time, r is the initial radius of the quartz particle, and α is the fraction of quartz converted.

With coarser grains (~138 μm) the transformation proceeds in 2 stages: in the first stage cristobalite nuclei are formed on the surface of the grains and in the second stage cristobalite formation proceeds into the bulk of the grains. The rate of reaction for the first stage is lower than for the second, but the duration of the first stage decreases steeply on raising the temperature (from 1270° to 1450°). The rate constant for the first stage includes the surface factor $1/r^2$; the rate constant for the second stage includes the quantity $3u/r$, and is therefore proportional to $1/r$.

When the quartz particles are fine, the rate constants of the two processes are comparable, and the reaction proceeds, as it were, at a constant rate from beginning to end. The kinetics of the transformation of quartz are altered by the presence of a mineraliser (which can be either in the solid or in the liquid state at the transformation temperature).

If the mineraliser acts in the solid phase, the transformation of the quartz is fast only in the immediate vicinity of the grains of the mineraliser: hence, the mineralising activity is of short duration, and the remainder of the reaction proceeds slowly by the mechanism which operates in pure quartz. Increasing the amount of mineraliser increases the amount of quartz converted in the initial period, but the rate of reaction in the final period is significantly lower.

If the mineraliser forms a liquid phase at the conversion temperature its influence becomes much more marked, because the area of contact with the quartz grains is increased by capillary action[100].

It should be noted that there is a significant difference between the temperatures of fast cristobalite formation of amorphous and of crystalline SiO_2. Thus, whereas Brazilian quartz is converted into cristobalite at temperatures of the order of 1500°, quartz glass and silicic acid gel convert even at 1200° (after 4–5 h).

This disparity between the crystallisation temperatures of crystalline and amorphous SiO_2 arises because bonds have to be broken in crystalline SiO_2 before cristobalite formation can occur, and the process is therefore more hindered and slower than crystallisation from the gel[83].

The transformation of quartz, quartz glass, or silicic acid gel proceeds with formation of an intermediate phase called metacristobalite[106–109]. Metacristobalite is rapidly converted into the stable cristobalite, but in the presence of the required concentration of alkali metal cations it is converted into tridymite. The reaction scheme is the following:

crystalline silica, quartz glass, silicic acid gel
↓
metacristobalite
↓
cristobalite

The density of metacristobalite is close to that of cristobalite, 2.30 g cm^{-3}, and is therefore identical to the density of the disordered phase formed by bombarding quartz with neutrons[97].

Chaklader and Roberts[110] have put forward a hypothetical scheme for the conversion of quartz into cristobalite, which was subsequently developed by Chaklader[76].

The high-temperature α-form of cristobalite changes to the low-temperature β-form on cooling, with an appreciable volume change.

It has been shown that the temperature of the $\alpha \rightleftharpoons \beta$ cristobalite transformation is a function of the thermal history of the sample, and usually lies[85,89] in the range 200–280°.

Cristobalite formed at relatively high temperatures also shows a higher transition temperature to the β-form. According to Flörke[70], the ideal cristobalite structure shows a threefold periodicity of layers of SiO_4 tetrahedra, which can be expressed as a structure of the type ABC | ABC | ABC. Cristobalite is often obtained in a different structure, including regions of twofold periodicity. This type of cristobalite has a lower $\alpha \rightleftharpoons \beta$ transition temperature.

The transition temperature can also show hysteresis, the transition from the high-temperature to the low-temperature form occurring 35° lower than the transition in the opposite direction[83].

VI. EFFECT OF IMPURITIES ON CRYSTALLISATION

The cristobalite formation process can be accelerated by a wide variety of foreign ions. The specific effect of alkali cations does not depend on the formation of a liquid phase, nor does it depend on their concentration, although it is now well established that the presence of a liquid phase can greatly activate the cristobalite formation process[63,64].

The transformation of quartz to cristobalite is induced by introducing cations into the quartz crystal lattice because the lattice is thereby deformed and the activation energy of the transformation is accordingly lowered. The deforming effect of the added ion is expected to increase with the ionic radius of the cation within any one group of the Periodic Table. Thus, the efficiency of K^+ towards cristobalite formation should be greater than that of Na^+ and that of Ba^{2+} should be greater than that of Sr^{2+}, Ca^{2+}, and Mg^{2+}, as has been experimentally confirmed.

Impurity ions also show different catalytic effects towards cristobalite formation in quartz glass, as was established by the systematic researches of Kainarskii, Degtyareva, and others. Kind and Makhlina studied the influence of various additives on the crystallisability of translucent fused quartz[105]. The impurities investigated were mainly oxides present in the sand as natural impurities, as well as some other oxides (B_2O_3, ZrO_2, P_2O_5). In every case it was found that alkali and alkaline-earth oxides had a negative influence, increasing in the sequence $Na_2O \rightarrow K_2O \rightarrow$ $\rightarrow CaO \rightarrow MgO$, and aluminium oxide had a positive influence. The crystallisability of the quartz samples was measured in a high-temperature gradient furnace in the region 1420–800°, for 24 h.

These measurements showed that practically all oxides, and the alkalis and alkaline earths in particular, increases the crystallisability of translucent fused quartz. The crystallisation of samples containing added Al_2O_3 was

unique: an addition of 0.05% inhibits the crystallisation, the effect increasing with concentration. The negative influence of the basic oxides and the positive influence of Al_2O_3 on the properties of translucent quartz glass are explained as follows. The ions of alkaline and alkaline-earth oxides are not glass-formers: they fill the voids in the three--dimensional network, thus altering and loosening the structure of the quartz glass and breaking Si–O bonds. Since very many defect sites are present, the viscosity of the glass in the softening temperature region decreases, and other properties also are affected.

The aluminium ion (Al^{3+}), having sixfold coordination, can behave as a glass-former under the right conditions and be incorporated in the three-dimensional glass network at a tetravalent SiO_2 site.

In this case one positive charge is lacking in order to satisfy the valence requirements: this can be provided, for example, by an Na ion. As a result, the points of attack created by the presence of Na ions in the quartz glass are neutralised. The Na ion is fixed in the vicinity of the aluminium ion without giving rise to a point of attack. The glass structure is stabilised, and the crystallisability is lowered. Beyond the optimum concentration the Al ion apparently remains in the six-fold coordination but behaves as a glass modifier rather than as a glass former. When Al_2O_3 is added to translucent fused quartz the coordination of the Al ion can change under certain conditions: this leads to neutralisation of the negative influence of alkali oxides.

According to Kainarskii and Degtyareva, the crystallisation of quartz glass is inhibited by the presence of 1.5% by weight of Al_2O_3,[64] whereas small additions of Al_2O_3 enhance the crystallisation.

VII. EFFECT OF ATMOSPHERE ON CRYSTALLISATION

The atmosphere used for heat treatment also plays an important part in the crystallisation process. Lipinski and Schwiete demonstrated the effect of different gaseous atmospheres during firing on the formation of cristobalite. Specially pure synthetic amorphous silica, containing no more than $2-3\times10^{-3}$% Na_2O, was investigated. The extent of crystallisation was measured at temperatures of 1200°, 1300°, 1400° in the following ambients: vacuum, air, N_2, O_2, Ar, CO_2, CO. The crystallisation was shown to be significantly retarded in a medium of Ar, N_2, or CO_2. For example, at 1200° in air crystallisation began after 2.5 h, but in an atmosphere of CO_2 the time needed was 32 h. At the same temperature, crystallisation is extremely slow in CO, CO_2, and Ar during the first 20–25 h, whereas it reaches 80% after 8 h in air[101].

The crystallisation of industrial quartz glass produced in the Soviet Union has been investigated. The samples were prepared from transparent vitreous mouldings which contained a large number of fine tapered channels due to the particular production technique. Crystallisation was induced at 1300° in an air atmosphere over a period of 10–15 h. A crystalline layer several tenths of a millimeter thick was obtained, and crystallisation occurred on the inner surfaces of the open channels as well as on the external surface of the sample, but not on the surfaces of the closed channels[104].

This observation is a clear illustration of the undeniable influence of atmosphere on the crystallisation of the glass.

In a vacuum of the order of 1×10^{-5} mmHg, however, crystallisation was not merely delayed but completely absent after 30–50 h treatment at 1300°. These experiments also provided ample indirect evidence that silica undergoes intensive dissociation in the region of its melting point, giving off free oxygen, so that the melt becomes oxygen-deficient and is partly reduced.

It was also established that glasses prepared by melting in high vacuum under identical conditions behave quite differently when subsequently heated in oxygen, nitrogen, hydrogen, and air. The role of oxygen and water vapour as the main activators of the crystallisation process was also confirmed.

The increase in weight during crystallisation, which can amount to 0.1%, can be taken as proof that the crystallisation process is indeed closely associated with chemical oxidation of the glass during conversion to cristobalite.

As a result of their experimental work, the authors came to the following conclusions.

The crystallisation of quartz glass is primarily a chemical process rather than a thermodynamic relaxation process. Crystallisation occurs when the glass gains enough oxygen to form the stoichiometrically much more perfect cristobalite. No crystallisation takes place unless the stoichiometric formula SiO_2 can be achieved by some method or other.

Fused quartz is a chemical compound of formula SiO_{2-x}, showing no tendency to crystallise under conditions which allow the retention of this non-stoichiometric composition.

The discrepancy between Lipinski and Schwiete's results for vacuum heat treatment and those of Boganov and coworkers must be stressed.

Whereas Boganov et al.[104] reported that cristobalite formation was completely suppressed, the other investigators found that crystallisation in a vacuum was even more marked than in air, but the quality of their vacuum was not stated.

The crystallisation process is affected also by a number of technological factors. Botvinkin and Zaporozhskii have described an investigation of pure quartz glass (containing $1-2\times10^{-2}$% of impurities) prepared by different methods (high-frequency, vacuum compression, and oxy--hydrogen)[3].

The first crystals visible under the microscope appeared on the surface of the gas-melted glass after 72 h heating at 1350°, whereas with glass samples prepared in contact with graphite (high-frequency and vacuum compression method) crystals first appeared after 2–2.5 h at the same temperature. Thus, the rate of generation of crystallisation centres is approximately 30–35 times smaller for the electrically melted glass than for the gas-melted glass.

It should be noted that the crystallisation conditions of pure amorphous or crystalline SiO_2 cannot be the same as those of quartz ceramics, because crystallisation can be speeded up by the porosity and the high degree of dispersity of the starting materials.

VIII. SINTERING AND ANNEALING

Sintering of quartz ceramics prepared from pure silica materials proceeds without the appearance of a liquid phase. In the presence of impurities, however, whether deliber-

ately added or already present in the material, a liquid phase can be formed. The sintering mechanism of quartz ceramics can be visualised as viscous flow and volume diffusion.

According to Frenkel'[111], solid-phase sintering occurs by "viscous flow", and can be resolved in time into two phases: (1) the coalescence of particles, leading to the disappearance of open pores (cavities) and to the formation of disconnected closed pores of various shapes (spherical in the simplest model); (2) the shrinkage of closed pores under the influence of surface tension forces.

The first stage of the process proceeds at a constant rate, depending only on the surface tension and on the viscosity of the medium surrounding the pore:

$$\frac{da}{d\tau} = \frac{3}{4} \times \frac{\sigma}{\mu},$$

where a is the radius of the pore, σ is the surface tension, τ is time, and μ is the viscosity coefficient at the given temperature.

During the second stage the rate of the process decreases continuously because of the retarding effect of the gas trapped in the pores. The theory of Frenkel' does not take account, however, of a number of special features of the sintering process in real powdery bodies, such as the wide variety of particle size, the presence of pores of different sizes, etc.

Pines has shown[112,113] that these factors are of major importance in the sintering process. In particular, powdery bodies of different particle size sinter in different ways.

Following Pines and other workers we may assume that the sintering of a real powdery body results primarily from bulk diffusion, but also partly from surface diffusion. The mechanism of sintering in the absence of a liquid phase thus amounts to redistribution of the material in the body by directed self-diffusion. Interesting discussions of the sintering process can be found also in the papers by Kuczyński, Kingery, Coble, and Johnson and Cutler[114-117].

When considering the sintering of amorphous or crystalline SiO_2 one should first of all take into account the allotropic transformations of the compound, which are ignored by all the existing theories of sintering. Data showing the appreciable effect of these factors are available.

Nishanova and coworkers[35] have studied the sintering of a quartz glass ceramic containing a fairly high concentration of impurities (99.44% SiO_2). Their samples were prepared by pressing at 800 kg cm^{-2} powder from a vibro-mill having a specific surface area of 3100–9800 cm^2 g^{-1}. The bulk density of the samples before firing was 1.41–1.44 g cm^{-3}, their porosity was 34.5–36%. Annealing was carried out in a Silit furnace and in a gas-fired furnace. The results are summarised in Table 2.

The samples annealed in the gas-fired furnace gave somewhat different results, which confirms the influence of the gaseous medium.

Thus, the maximum strength was observed at 1250°, and further increase led to crystallisation. Somewhat greater densities and linear shrinkage factors were obtained in the gas-fired furnace.

The same workers also heat treated samples prepared by slip casting from a mass containing a granular filler. The filler, of fused quartz, included 0.25–0.5 and 0.5–

TABLE 2. Influence of degree of comminution of the powder and of firing temperature in a Silit furnace on the sintering and crystallisation of specimens.

Specific surface area, cm^2 g^{-1}	Firing temperature, °C	Linear shrinkage, %	Density, g cm^{-3}	Apparent porosity, %	Strength under compression, kg cm^{-2}	Flexural strength, kg cm^{-2}	Cristobalite content, %
3100	1150	0.2	1.45	34.1	31	17	0
	1200	0.2	1.45	34.2	100	48	0
	1270	2.2	1.53	30.8	359	94	<1
	1300	3.1	1.55	30.0	—	74	3
	1350	3.9	1.58	30.5	—	56	51
9800	1150	0.5	1.47	33.2	104	45	0
	1200	3.7	1.58	28.5	326	94	0
	1270	5.8	1.73	21.8	673	187	<1
	1300	9.0	1.86	16.9	—	179	5
	1350	9.2	1.88	16.8	—	117	63

1 mm fractions, and accounted for 30–50% of the total. Under these conditions the strength under compression reached 460 kg cm^{-2}. Summarising the findings of this paper, we note the rather low mechanical strength both under bending (up to 270 kg cm^{-2}) and under compression (up to 1490 kg cm^{-2}), due no doubt to low initial density and to the rather coarse size distribution.

Popil'skii and Nishanova[42] also investigated the sintering of pressed specimens (5 × 5 × 50 mm) under a specific pressure of 800 kg cm^{-2}. The starting material was translucent quartz glass (99.9% SiO_2). Grinding was done in a vibro-mill (dry method) or in ball mill (wet method) to a specific surface area of 10 000 cm^2 g^{-1}.

Sintering was continued for 2 h at temperatures of 1100°, 1150°, 1200°, 1250°, and 1300°. All the fired specimens showed high porosity, relatively low strength, and in most cases a linear thermal expansion coefficient higher than that of silica glass.

The authors concluded that samples prepared from wet-milled quartz glass (whether transparent or translucent) exhibit slow sintering and crystallisation, but they were unable to explain this effect. They also reported that 0.15% iron contamination has no particular influence on sintering and crystallisation.

From the results set out in Table 3, summarising the measurements of sintering, crystallisation, and strength on specimens made from all the starting material examined, we may conclude as follows.

TABLE 3.

Paste No.	Treatment of starting material	Porosity, % at cristobalite temperatures, °C					Coefficient of thermal expansion $10^6\ \alpha_{mean}$ in the range 20–400 (% in brackets) at cristobalite temperatures, °C					Flexural strength, kg cm^{-2} at cristobalite temperatures, °C				
		1100	1150	1200	1150	1300	1100	1150	1200	1250	1300	1000	1150	1200	1250	1300
	Transparent quartz glass															
1	Vibro-mill 180 min	31.5	16.3	13.8	11.9	9.1	0.54	1.42	4.04	33.54 (78)	37.54 (82)	65	310	210	195	105
2	Vibro-mill 180 min, washed	31.2	17.0	16.1	13.8	10.0	0.54	1.01	23.84	37.54 (83)	38.54 (85)	165	355	150	130	160
3	Wet mill, washed	45.9	36.1	33.5	15.6	10.2	0.54	0.65	1.39	20.94 (44)	37.94 (86)	30	170	305	145	170
	Translucent quartz glass															
4	Vibro-mill 180 min	37.5	34.5	32.4	22.0	19.8	0.54	0.54	0.54	0.72	8.94	—	55	65	330	130
5	Vibro-mill 180 min, washed	34.0	32.0	27.1	17.8	11.8	0.54	0.54	0.54	1.44	21.84	40	105	180	340	175
6	Wet mill, washed	35.8	35.8	34.2	29.5	16.0	0.54	0.54	0.54	0.54	6.29	—	—	30	140	260

If we scrutinise the results from the standpoint of a minimum coefficient of thermal expansion, we note that specimens with a low expansion coefficient (0.54×10^{-6}) show a porosity of 31.5–45.9% (for transparent quartz glass as the starting material) or 32.4–34.2% (for translucent quartz glass); the strength under bending varies from 30 to 165 kg cm^{-2} and from 30 to 180 kg cm^{-2} for the two cases respectively.

If maximum mechanical strength is the criterion, specimens made from sintered transparent quartz glass and having a strength of 305–310 kg cm^{-2} exhibit a thermal expansion coefficient between 1.01×10^{-6} and 1.42×10^{-6}, i.e. higher than the expansion of fused quartz glass by a factor of 2–3; the porosity under these conditions is 16–33%. The corresponding values for specimens from translucent quartz glass of strength 260–340 kg cm^{-2} are $6.29 \times \times 10^{-6}$–$0.72 \times 10^{-6}$; the porosity is 16–22%.

Therefore, the results are unsatisfactory as regards optimising this set of properties in specimens made by any particular regime. Thus, the thermal stability (an essential property of this material) falls off as the thermal expansion increases. However, the low mechanical strength and the high porosity of samples having a low thermal expansion can impair the thermal stability and also various other properties.

Walton showed that the mechanical strength of quartz ceramics is raised by a small amount of cristobalite formed during firing (Fig. 6). He suggests that very small particles begin to crystallise during firing, and are converted into cristobalite. Since these fine particles are distributed throughout the bulk, a very intimate binder of cristobalite is formed and causes incipient sintering during the firing operation: in other words, cristobalite appears between the coarser grains of the remaining fused quartz and acts as a binder for these grains.

However, in view of the higher sintering temperature of cristobalite, the suggestion that sintering of this material can occur at 1250° is unconvincing.

It may be thought that a small amount of cristobalite surrounded by a mass of amorphous quartz will not raise the thermal expansion coefficient to the value calculated by assuming additive behaviour, because the expansion of the microscopic cristobalite centres can be checked by the substrate.

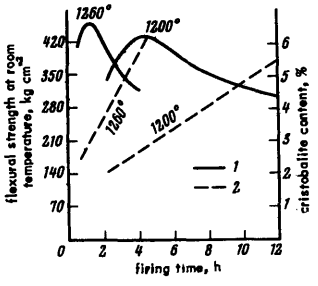


Fig. 6. Variation of the strength of a quartz ceramic with firing time and with cristobalite content:
1) limiting flexural strength; 2) cristobalite content.

A method of producing quartz ceramics from fused quartz has been patented[37], which prevents the formation of cristobalite by the addition of finely divided B_2O_3 to the starting composition, in conjunction with a protective gas atmosphere during sintering.

The amount of B_2O_3 added as a fine powder (up to 2–4 μm particle size) should be at least 1.2% of the weight of SiO_2; the mass to be formed is then prepared by a standard method. Firing must be done in a tightly sealed capsule or in a medium of quartz sand to prevent direct access of furnace gases. The firing temperature can be higher than the normal firing temperatures for quartz ceramics (up to 1350°). The firing time is 30 min. Sintering in a hydrogen atmosphere or in an atmosphere containing vapours of boron compounds produces good results.

Water vapour has been shown[47] to have a distinctly beneficial effect on the sintering of quartz ceramics. However, since water vapour also catalyses the crystallisation of amorphous SiO_2, the onset of cristobalite formation is lowered to 865° by water vapour[101].

The sintering of quartz ceramics to high relative densities without degrading the properties of the articles obtained is complicated by the devitrification phenomena leading to cristobalite formation discussed above. This accounts for the rather high porosity of quartz ceramics, which has an unfavourable effect on the properties. According to published data, the porosity of quartz ceramics varies between 10 and 30%.

To achieve high levels of sintering it is essential to take account of factors such as the density and particle size distribution of the preparation. Under otherwise similar conditions, a denser raw material and a finer granular composition lead to faster sintering at a given temperature. The variation of porosity and density after firing with the density and the porosity of the raw material is illustrated in Fig. 4.

The present writers[45] have demonstrated the profound effect of the state of comminution of the starting material on the sintering of fused-quartz ceramics. Fig. 7 shows the variation of the apparent porosity of specimens made by slip casting at firing temperatures of 1200° and 1250° with firing time, for different mean surface diameters d_{mean} of the particles (calculated by the formula given in Section III of this paper).

We have also shown[45] that a quartz-glass ceramic with zero apparent porosity can, in principle, be prepared, and that the strength and thermal expansion coefficient of this

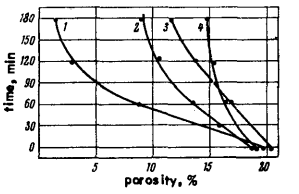


Fig. 7. Variation of apparent porosity with firing temperature and time and mean particle size:
1) firing temperature 1250°, d_{mean} 1 μm;
2) firing temperature 1250°, d_{mean} 2.5 μm;
3) firing temperature 1200°, d_{mean} 1 μm;
4) firing temperature 1200°, d_{mean} 2.5 μm.

material are close to those of quartz glass. The necessary conditions are: small particle size (60–70% of the particles below 5 μm), a very dense starting material (12–15% porosity), and firing at 1300–1450° for times varying from 1.5–2 h to 10–15 min according to the temperature.

The sintering of crystalline silica also is of interest. Dietz and Schulle[17] have investigated the sintering of quartz and cristobalite powders as a function of purity, particle size, temperature, and time. Pure cristobalite was obtained by firing powdered rock crystal at 1530° for 5 h. Specimens of the moistened powders were pressed at 1300 kg cm^{-2}. Quartz began to sinter at 1250°, as shown by an increase in strength and density.

Above 1450° a loss of strength was observed, and this was ascribed to the conversion of quartz into cristobalite. Cristobalite begins to sinter at temperatures beyond 1450°, but the effect of sintering on cristobalite is less marked than on quartz.

The sintering of siliceous materials proceeds in the solid phase, and the formation of a liquid phase as a result of the presence of impurities is of secondary importance. Dietz and Schulle[17] explain the densification and the increase in strength of the quartz by invoking an intermediate amorphous phase, formed during the transition of quartz to cristobalite induced by the mineralising effect of impurities. But this cannot account for the sintering of cristobalite, because no intermediate phase is formed in this modification of silica. The possibility of diffusion processes influencing the sintering of quartz and cristobalite is not excluded.

According to other workers[118], the decrease in porosity and the binding of quartz particles begins at 1580°, and sintering begins at 1605°. At 1620–1660° sintering is fast, and the pores between particles disappear. At 1660° the quartz crystals are converted into optically active cristobalite.

Chaklader and Roberts[110] examined specimens of pure (99.96% SiO_2) quartz, and observed intensive sintering during the first few hours' heating at 1500–1570°, followed by a loosening of the structure. Fig. 8 shows the strength under compression as a function of the time of heat treatment at 1570°. The loss of strength is due to the cristobalite transition undergone by the specimens. The authors suggest the following sintering mechanisms: surface or bulk diffusion, plastic flow, evaporation, or condensation. Sintering apparently occurs through a disordered surface layer on grains formed at high temperatures. Appreciable sintering is observed as soon as the transition phase is formed.

The sharp decrease in strength of the sintered specimens is explained by the formation of significant amounts of cristobalite, which does not sinter at these temperatures. The sintering process is explained by a mechanism involving the transformation of quartz into cristobalite. The expansion observed in the early stages of firing is the result of the conversion of quartz (density 2.65 g cm^{-3}) into a transition phase (2.30 g cm^{-3}) which is amorphous and has vitreous properties.

As soon as a thin layer of the transition phase is formed on the surface of the quartz particles, these particles tend to coalesce, and the strength accordingly increases. The shrinkage is due to the transfer of material to the pore volume. Necks are formed at the points of contact between particles under the influence of capillarity forces.

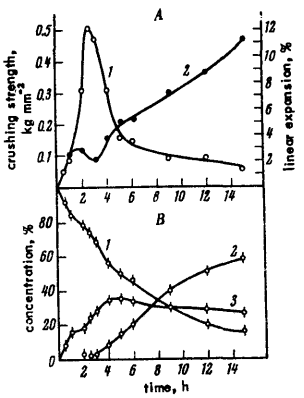


Fig. 8. Variation of crushing strength and relative amounts of quartz, intermediate phase, and cristobalite as a function of firing time of quartz specimens at 1570°.
A: 1) linear expansion in %; 2) crushing strength in kg mm^{-2}.
B: 1) quartz; 2) cristobalite; 3) intermediate phase.

A critical survey of available data on the sintering of crystalline silica, fused quartz, and amorphous synthetic silica leads to the following general propositions.

The occurrence of sintering and the sintering temperature are invariably associated with incipient crystallisation. The lower the temperature at which crystallisation of any particular form of silica begins, the lower will be the temperature of incipient sintering. There is also evidence that intense sintering occurs during the period immediately prior to crystallisation, i.e. during the stage of formation of metacristobalite. We have shown[45] that the specific gravity of a densely sintered ceramic made from fused quartz is often slightly higher than that of fused quartz (2.21 g cm^{-3}), suggesting partial conversion into metacristobalite not involving appreciable degradation of the properties. The method of formation and the pretreatment of the material also have an undeniable effect on the onset and on the kinetics of the sintering process.

In order to achieve higher densities in a ceramic based on fused quartz without at the same time causing the formation of cristobalite it is desirable to use finely milled powders. In this way the rate of sintering is increased more than the rate of onset of crystallisation. Conversely, coarser granular compositions retard the onset of crystallisation, but since sintering is very slow and much longer firing times are needed the amount of crystallisation is relatively large.

The initial density of the raw material plays an important part in quartz ceramics, high initial densities allowing extremely dense materials to be produced.

When specifying the firing schedule of an article it is important first of all to consider the possibility of cristobalite formation. The initial particle size distribution and the presence of impurities are also extremely important.

Fig. 9 summarises our results[45] on the effect of time and temperature on the onset of cristobalite formation for specimens prepared by slip casting from fused quartz containing 99.9% of SiO_2.

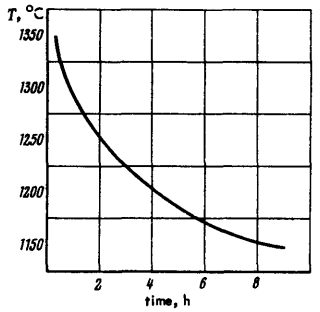


Fig. 9. Variation of the onset of crystallisation with temperature and time.

The maximum firing temperature is 1650–1680° for articles made from quartz sand, and 1250–1300° for articles made from fused quartz, The time of treatment at the maximum temperature is usually 1 h, but equally good results can be obtained for shorter times at higher temperatures.

Schulle and Ulbricht[24] have described the following firing schedule for articles made by slip casting from quartz sand. The specimens were heated at 1000° for 3 h in a Silit furnace before being subjected to the required firing temperature (1680°). After the prescribed firing time the specimens were removed from the furnace and placed in a cooling oven set at 900°, in which they were allowed to cool to room temperature.

Fleming[20] considers that 4 h at 1200° is sufficient for relatively small articles made of fused quartz, whereas larger articles need 1 h at 1260°.

The shrinkage during firing depends on the porosity of the starting preparation and on the maximum temperature and time of heat treatment, and is usually in the range 0.5–5%. With large articles there is a possibility of distortion of the lower parts.

IX. SURFACE IMPREGNATION AND SEALING

Quartz ceramics offer good electrical properties, similar to those of quartz glass. However, the unavoidable porosity associated with the conventional ceramic production techniques has an appreciable effect on the electrical properties. Furthermore, quartz ceramics have inadequate moisture resistance. In a number of applications both high density (absence of porosity) and moisture resistance are essential. However, the achievement of adequate density by sintering is made difficult by the cristobalite transformation discussed above.

In this connection, the following methods for achieving the required properties have been proposed: impregnation, glazing, surface melting, and hydrophobic coatings[31-33]. Impregnation consists, essentially, of soaking the fired porous article in a solution which can fill the pore volume and subsequent deposition of a solid phase from the solution. The rate, uniformity, and completeness of the soaking treatment depend on a number of factors: the magnitude of the surface tension at the interface between the impregnating solution and the body, the size and shape of the pores in the sintered article, and the viscosity of the penetrating solution.

The impregnation method has already been used in practice for powder-metallurgy articles. For example, porous sintered iron or steel is usually impregnated with various metals and alloys, mostly based on copper. In this application the sintered articles must be impregnated with much more fusible metals.

In the preparation of ceramic materials impregnation problems have attracted little attention so far, and the work discussed below is based exclusively on laboratory data[24,31-33].

The theoretical foundations of impregnation have been developed by Deryagin[119]. The basic postulates of his theory are essentially the following.

Let an element of the impregnation front move to a new position in a given time, filling a pore volume ΔV with a wall surface of ΔS:

$$p\,\Delta V = A\,\Delta S,$$

where p is the pressure drop across the layer l of impregnated volume due to the internal friction of the liquid and A is the specific work of wetting. Then,

$$l = k\frac{\Sigma}{\delta^2}\sigma\cos\theta,$$

where l is the thickness of the impregnated layer, k is the filtration coefficient, δ is the fractional pore volume, Σ is the specific surface area of the impregnated body, σ is the surface tension of the liquid, θ is the limiting contact angle.

Impregnation is carried out after a preliminary heat treatment, and is followed by drying and firing. The best results are obtained in practice by impregnating with true solutions of inorganic materials. Colloidally disperse silica does not give good results because of the very small pore diameter of quartz ceramics, which acts as a filter and removes the most finely dispersed colloids after a thin layer has been impregnated. Impregnation is achieved by using hydrolysed ethyl silicate: the concentration is adjusted so that the silica is held in solution low enough to ensure complete impregnation of the ceramic, whereupon the ethyl silicate forms a gel which deposits SiO_2 in the pores.

However, since these gels are aqueous, some residual porosity is unavoidable to allow the passage of the dehydration products during firing, and the method allows the porosity to be decreased but not completely eliminated.

When the porosity of the original ceramic is high, impregnation affords a significant improvement in strength and decrease in porosity[24].

As the porosity of the ceramic decreases, impregnation becomes slower. An aqueous solution of aluminium chloride has been examined as a possible impregnating agent[33]. Aluminium hydroxide was precipitated in the pores of the quartz ceramic by altering the pH. This material reacts with silica during sintering, forming mullite. However, since mullite is formed at temperatures above the crystallisation temperature of quartz ceramics, we are faced with the problem of avoiding the conversion of fused quartz into cristobalite and yet producing mullite, which can be sintered sufficiently to eliminate the porosity.

Glazing of quartz ceramics is difficult because of the very low thermal expansion coefficient of the material, which necessitates a glaze having either zero or a small negative thermal expansion coefficient.

Glazes of materials such as spodumene and petalite, which satisfy these requirements, have a flow temperature higher than the crystallisation temperature of quartz ceramics, and cannot be applied by ordinary methods. However, the glazes can be deposited by flame-spraying whilst retaining their low or negative thermal expansion coefficient. Surface sealing can be achieved also by fusing the surface layer of the glass ceramic with a plasma torch.

Both glazing and surface melting must be carried out whilst heating the ceramic to 1000–1100° to avoid large thermal stresses, and the article must then be annealed.

Hydrophobic coatings which are fired in flight by the temperature rise can be used for sealing antenna fairings [31].

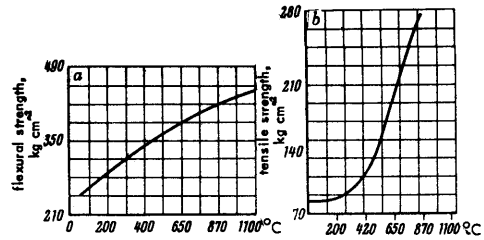


Fig. 11. Effect of temperature on the mechanical strength of quartz ceramics:
(*a*) flexural strength; (*b*) tensile strength.

X. PROPERTIES AND APPLICATIONS OF QUARTZ CERAMICS

Quartz ceramics made from fused quartz possess many of the valuable properties of the starting material: a low coefficient of thermal expansion, good high-temperature stability, good electrical parameters, high chemical stability. However, quartz ceramics also exhibit some properties which are not present in fused quartz (quartz glass). Unlike quartz glass, whose thermal conductivity rises quite significantly with temperature, quartz ceramics and quartz ceramic foams have a constant and fairly low thermal conductivity over the temperature range up to 1100°. As Fig. 10 shows, the thermal conductivity of quartz glass at 500° is approximately 5 times higher than that of quartz ceramics and 20 times higher than that of quartz foam.

A steep rise in the thermal conductivity of quartz ceramics is observed in the temperature region above 1100°, due to the formation of cristobalite. Furthermore, devitrified quartz glass breaks down on cooling, whereas the ceramic can retain its shape. A special feature of quartz ceramics in comparison with other types of ceramic is the increase of tensile and flexural strength with temperature, evidently associated with an increased plasticity and a lower brittleness [18,52]. The increase in strength is quite significant: as Fig. 11 shows, the strength under bending is much higher at 1100°. [18]

Another distinguishing feature of quartz ceramics as compared with other ceramic materials is their much smaller shrinkage both on drying (0.1–0.5%) and on firing.

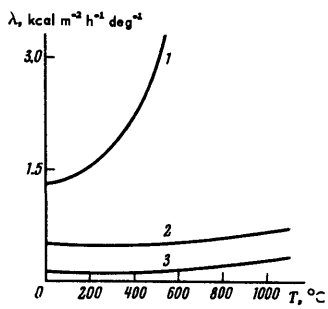


Fig. 10. Temperature dependence of thermal conductivity:
(1) transparent quartz glass, (2) quartz ceramic, and (3) quartz foam.

The main structural difference between quartz ceramics and quartz glass lies in their porosity, from which stem all the other differences in mechanical as well as electrical properties.

The influence of porosity on the mechanical, thermal, and dielectric properties of quartz ceramics has been investigated [46]. Specimens prepared by slip casting, hot pressing, and spray coating were divided into four groups: low (25–40%), intermediate (30–70%), high (85–90%), and very high (90–100%) density as compared with the theoretical density. It was shown that the properties of the ceramic depend on the type of raw material and on the method of preparation as well as on the pore volume, with the exception of the dielectric properties, which are determined exclusively by the porosity. The strength is as much a function of the method of forming as of the porosity.

The porosity of quartz ceramics is responsible for the low thermal conductivity of these materials, for their low mechanical strength (relative to that of quartz glass), and for the slight difference in electrical resistance. The ceramic, unlike quartz glass, is not transparent (having a white colour), and has a lower specific gravity. However, when the porosity is minimised (to the 1–2% level) the basic properties of the ceramic become almost identical to those of the glass.

Quartz ceramics have some advantages over other materials which have been considered for use in missile cones. Their dielectric constant at 10^{10} Hz should not vary by more than ±5% between room temperature and the maximum, and the tangent of the dielectric loss angle under these conditions should be less than 0.01. [31]

Of the three materials: quartz ceramic, corundum ceramic, and Pyroceram 9606, a ceramic made from fused quartz satisfies these requirements most fully [31,52].

Furthermore, rocket cones made by slip casting from fused quartz are much cheaper to produce [52] than those made from Pyroceram or Al_2O_3. Their flexural strength increases with temperature (by 33% at 1100°), as compared with a 67% decrease for Al_2O_3 and a 25% decrease for Pyroceram [52]. It has even been suggested [33] that articles can be made more cheaply in quartz ceramics than in fused quartz. Porous quartz insulators are used also in radar installations.

Many fields of application require high thermal stability, constancy of dimensions, low thermal conductivity, and other important properties: quartz ceramics satisfy these requirements fully. Quartz ceramics can be used in the newer technological areas, such as missile and nuclear technology, and also as general purpose refractories.

The devitrification of quartz ceramics at temperatures above 1100° does not exclude the use of these materials at the higher temperatures: the permissible concentration of cristobalite is determined by the specific conditions of use of the article. An important consideration is the duration of the exposure to the maximum temperature. Studies of the suitability of quartz ceramics for thermal shielding systems and for the manufacture of aircraft components have shown that quartz ceramics are the most promising material for these purposes. Among the articles which could be manufactured from quartz ceramics the following are listed: front flanges and nose cones for rockets, antenna fairings, nozzles for rocket engines, etc. In addition to their excellent dielectric properties, quartz ceramics offer a high thermal stability and low thermal conductivity, which make them suitable for these applications [31-33].

A rocket cone 61 cm in diameter and 1.22 m high has been made by slip casting. Its wall thickness was so uniform that no further mechanical operations were needed [36].

When a missile re-enters the denser layers of the atmosphere the temperature rises well above the melting point of quartz, and can reach 2500°. However, since the passage through the dense layers is of short duration, and the material has a high viscosity, the rate of wear of the nose cone is only ~0.025 mm s^{-1}.

The nose cone of the U. S. Titan intercontinental ballistic missile is an example of the use of quartz ceramics in space technology [49].

Quartz foam, which is used as a heat shield, is a very promising material for applications in aerospace technology [43,44]. In order to increase its mechanical strength, quartz foam is impregnated with organic resins [44].

Heat shields are also used for the nose cones of rockets in order to give reliable protection to the electronic systems against heat and radiation during passage through the dense layers of the atmosphere [29]. Rare-earth elements or their oxides are added to the fused quartz. The most favoured is gadolinium, or the other rare-earth elements with similar properties (La, Ce, Pr, Nd, Eu, Tb, Er, etc.). The concentration of the additive is kept between 0.1 and 10%. and this determines many of the properties of the shield. When nuclear radiation is present gadolinium is to be preferred, because it has the property of absorbing radiation. Without the addition of rare-earth elements, infrared radiation and heat are readily transmitted from the outer surface of the quartz layer to the inner regions when the nose cone is subjected to heating. However, the rare-earth elements cause absorption and back radiation from the outer layers of the nose cone.

In order to assess the properties of quartz ceramics, their ablation properties have been evaluated with an electric arc whose temperature was stabilised with air or water [32]. The specimen used for the test was cylindrical, with one hemispherical end. The rate of ablation was assessed by monitoring the rate of decrease in the length of the specimen whilst the arc discharge was applied. The experimental results and the working parameters of the test are summarised in Table 4.

Foamed quartz ceramics make high-grade reflectors of infrared radiation. This is because the outer layer of the quartz foam reaches a high temperature almost as soon as the lamps are energised and generates energy which is absorbed as infrared radiation. Furthermore, the underlying layers of the quartz foam greatly obstruct the transmission of infrared rays.

TABLE 4. Ablation data for quartz ceramics, obtained by plasma torch spraying.

Type of arc	Air stabilised	Water stabilised
Power, kW	100	60
Specimen diameter, mm	12.7	19
Gas velocity	Mach 2.5	100–1000 m s^{-1}
Duration of test, s	25	20
Ablation, cm	1.2	0.78
Rate of ablation, cm s^{-1}	0.048	0.039

Quartz ceramics are used in the manufacture of electrical insulators and of fairings for radar aerials. Ceramic insulators of any shape can be made by slip casting. After firing, these are impregnated with a synthetic resin or lacquer to eliminate the porosity.

Fig. 12 shows the temperature variation of electrical resistance of ceramic specimens, both with and without silicone varnish impregnation, as well as tan α and ϵ.

To test the possibility of using quartz ceramics as insulators in high-temperature nuclear reactors, a series of quartz rods was cast and fired at 1380° for 48 h in order to form cristobalite [19,33]. Another batch of rods, earmarked for studying the influence of neutron irradiation on the strength of quartz ceramics, was fired at 1260° for 1 h.

The quartz ceramic specimens were irradiated in an experimental reactor with a neutron flux of energy 816 mV r. Complete collapse of the cristobalite structure to the amorphous state was observed at a dose of about 4×10^{20} neutrons cm^{-2} s^{-1}. No permanent changes in flexural strength were noted in any of the irradiated specimens.

Fused quartz does not undergo changes under the influence of nuclear radiation, and has a small capture cross-section for thermal neutrons: this is why the material is used for containers in experiments involving radiation.

Irradiation with a dose of $\sim 2 \times 10^{20}$ neutrons cm^{-2} s^{-1} has little effect on the strength of quartz ceramics, which varies within the range ±10%.

The possibility of using a ceramic made from fused quartz in the atomic energy industry as a medium for fuel elements in the SiO_2–UO_2 system has been investigated. It

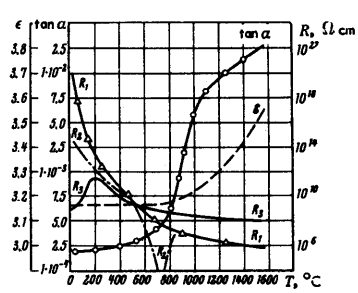


Fig. 12. Temperature dependence of the electrical resistance of quartz glass (R_1), impregnated (R_2), and non-impregnated (R_3) quartz ceramics, of the tangent of the dielectric loss angle (tan α), and of the dielectric constant (ϵ) of quartz ceramics.

was shown that these materials satisfactorily retain the gaseous fission products and are highly stable towards the breakdown caused by the recoil of fission products[19]. Quartz bodies prepared by casting and quartz foam should find widespread use as materials for thermal insulation in nuclear reactors.

The following applications may be quoted as examples of the use of quartz ceramics as refractories: dies for hot pressing, fixtures for rigidly welding cellular constructions of stainless steel, pipes for conveying molten aluminium, etc.

One of the applications of quartz ceramics is the monolithic lining of boilers: high-grade refractories were previously used for this purpose, but their life was limited to three months by temperature drops and by mechanical vibrations[33], whereas linings of quartz ceramic give service for upwards of two years. Another example of the use of quartz ceramics is in the lining of roasting kilns. Panels 122 × 152 × 15 cm in size were cast from a mass made from fused quartz, and used in the kiln assembly after being dried but in the unfired condition. The performance after one year's use of the kiln was satisfactory, although the temperature drop from the hot to the cold side of the blocks was of the order of 1000°.

Ceramic foam has been used for lining crucible furnaces for melting aluminium, with a resulting fuel saving of 50–60% as compared with the conventional refractory lining[33].

Quartz ceramics can be successfully applied to the production of casting moulds for repeated use[20,21]. To investigate the effect of devitrification, an iron melt was cast into a mould made of quartz ceramic (from fused quartz) and allowed to solidify completely. After 12 such cycles, no sign of crystallisation was observed in the material. It was also found that if the first cycle did not induce the onset of devitrification, the subsequent cycles also failed to bring it about.

TABLE 5. Properties of quartz glass, quartz ceramic, and foamed quartz ceramic.

Parameters	Quartz glass	Quartz ceramic	Foamed quartz ceramic
Density at 20°, g cm^{-3}	2.21	1.82–2.15	0.4–0.7
Overall porosity, %	0	1–20	50–60
Limiting strength at 20°, kg cm^{-2}			
crushing	5000–10 000	2500–5000	500–700
flexural	700–800	200–600	14–35
tensile	230–400	140–210	—
Limiting strength under impact bending, kg cm^{-2}	0.85–1.0	0.8–1.8	—
Thermal expansion coefficient, deg^{-1}, × 10^6	0.54	0.54	0.54
Thermal conductivity, kcal h^{-1} deg^{-1}			
at 0°	1.0–1.2	0.5	0.1
at 1200°	—	0.8	0.5
Specific heat, cal g^{-1} deg^{-1}, × 10^3 at 0°	200	200	—
Softening temperature under a load of 2 kg cm^{-2}, °C	1250	1250	1250
Dielectric constant			
at 20°	3.7	3.2–3.6	—
at 1000°	—	3.3–3.7	—
Tangent of the dielectric loss angle in the frequency range 30 kHz–10 MHz			
at 20°	6×10^{-4}	2×10^{-4}	
at 800°	6.7×10^{-4}	6×10^{-4}	
at 1200°	8×10^{-2}	8×10^{-2}	
Total linear shrinkage after drying and firing, %		1–6	1–6
Microscopic absorption cross-section for thermal neutrons at 2200 m s^{-1}	—	0.26	—
Macroscopic absorption cross-section for thermal neutrons at 2200 m s^{-1}	—	0.057	—
Relative slowing down	—	1.29	—

In another experiment one size of a quartz ceramic block was exposed to a high furnace temperature whilst the other side remained cold: the hot side crystallised at 1090°, but the crystallised regions were firmly bound by the uncrystallised substrate, as shown by a vibration test[31].

The main properties of quartz glass, quartz ceramics, and quartz ceramic foam are listed in Table 5.

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Quartz ceramics can be manufactured by slip casting, slip foaming, hot pressing, semi-dry pressing, and various other methods from fused quartz, synthetic amorphous silica, and quartz sand.

Devitrification of the articles, which occurs at the maximum firing temperatures, can impair the thermal stability if it reaches appreciable proportions; however, by choosing the most appropriate firing schedules, the formation of cristobalite can be avoided or limited to low amounts.

The property of quartz ceramics which distinguishes them from other types of ceramic is their low coefficient of thermal expansion and their unusually high thermal stability. Compared with quartz glass, quartz ceramics have a significantly lower thermal conductivity (especially at high temperatures), and they do not break up as a result of cristobalite formation.

Quartz ceramics may find wide applications in the heat-resisting members of missiles, in nuclear technology, in the chemical and metallurgical industry, and as general purpose refractories.

Some specific features of the production of quartz ceramics must be pointed out. Devitrification during sintering is a complicating factor in the production of a densely sintered ceramic. It is therefore desirable to start from specially prepared fused quartz, which has a lesser tendency to form cristobalite (gas melting, avoidance of impurities conducive to crystallisation, etc.). It is important to maximise the density of the stock in order to assist sintering. Increasing the density of the ceramic can improve the physical and electrical properties of these materials very considerably.

Doping the quartz with rare-earth elements offers interesting possibilities because these elements can improve many of the properties of quartz.

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STUDIES OF POLYMER SOLUTIONS CARRIED OUT IN POLAND

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The field of studies on polymer solutions is very extensive and covers a wide range of varied problems. Such studies may be carried out with various aims in view — to define the properties of the solutions, or to characterise the macromolecules themselves from the properties of the solutions. Because of the variety of problems raised it is not possible to cover completely all work on the study of polymer solutions.

In order that the material presented shall be treated as fully as possible we shall consider only two questions, namely the determination of molecular weight and the study of polydispersity. We shall also examine some interesting papers on the hydrodynamics of solutions, and certain others.

In Polish literature on molecular weight determination, problems of practical importance arouse greatest interest. These papers generally describe experimental studies. The number of theoretical papers on this problem is much smaller.

Most attention has been paid to viscometric studies, and second place, as far as number of papers is concerned, is taken by work on procedures using the ultracentrifuge.

Papers on the determination and calculation of average molecular weight by osmometric and cryoscopic methods and from terminal groups are fairly numerous. There are fewer papers on light scattering by polymer solutions, and they have begun to appear only recently. There are also some papers which discuss the possible use of procedures which have not yet found such extensive application as those noted earlier.

The viscometric method, which requires simple apparatus, is the most convenient method for determining the molecular weight of polymers. It is becoming the most commonly used method of control in industry. The interest of Polish authors in this method is determined to a considerable extent by the practical approach.

Among the large number of papers in this field, mention may be made of the comparatively early determinations, the first to appear in the scientific literature, of the viscometric relationships for polyethylene terephthalate[1]. Tursa and Skwarski determined the molecular weights of a number of low-polymer polyterephthalate fractions by a cryoscopic method and, with the aid of viscometric data, they calculated the constants of the Mark–Houwink equation for the system studied.

Among recent work, mention may be made of a paper by Nadziakiewicz and Jedlińska[2] of the Lodz Synthetic Fibres Institute, devoted to methods of determining the degree of polymerisation of cellulose in solvents in which it does not undergo degradation under the influence of atmospheric oxygen. On the basis of published data and their own studies, they concluded that ethylenediaminecadmium hydroxide has a number of advantages as a solvent for cellulose. Overcoming difficulties in the procedure, associated with the low solubility of some forms of cellulose, the authors confirmed that the viscosity of the solution is linearly dependent on the degree of polymerisation in the range studied, and derived the viscometric equation.

Several other papers[3,4] have been devoted to studies of the dependence of the viscosity of solutions of cellulose in other solvents on the degree of polymerisation.

The viscosity of solutions of other polymers was studied by Kryszewski[5], Skwarski[6], Orszagh[7], Łaszkiewicz[8], and others.

Problems new to the scientific literature in this field were raised by Połowiński[9,10] of the Physical Chemistry of Polymers Faculty in Lodz Polytechnical Institute. Poło-

winski studied the dependence of the viscosity of solutions of graft copolymers on their molecular weight, carrying out the experiments using graft copolymers with accurately determined molecular structure. He suggested that when the solvents used are "good" solvents for the polymers present in the copolymers, the viscometric data can be explained on the basis of the theory of the viscosity of solutions of branched polymers, developed by Berry and Orofino. The premise adopted was confirmed experimentally.

Among these papers mentioned briefly, particular attention may be drawn to several devoted to the development of apparatus. These include papers on viscometers with replaceable capillaries[11], air-tight seals[12], and electronic control of the duration of flow of liquid, giving very high accuracy in the measurements[13], and modifications of a viscometer[14] in which dilution of the solution is carried out.

In addition to these papers, dealing directly or indirectly with the viscometric determination of the molecular weights of polymers, there is a fairly large number of papers describing studies of the viscosity of polymer solutions from another viewpoint. Because of space limitations, we merely cite these papers without giving details[15-31].

Studies using the ultracentrifuge to determine the molecular weight of polymers and the determination of polydispersity by sedimentation analysis have been carried out in Poland in only one research institute, namely the Scientific Research Institute of the "Oświęcim" Chemical Plant. Some papers have been devoted to a discussion of the applicability of the equations derived by various authors, particularly the Flory–Mandelkern equation, for the determination of molecular weights by the centrifuge method[32-34]. In some papers the results of the discussions were compared with the author's own experimental results. The materials studied were polycarbonates and copolymers of butadiene.

Most authors have dealt with methods for determining the average molecular weight.

In the field of osmometry, the following may be mentioned: a methodological paper by Marciniak and Szota[35] on measurements at elevated temperatures; a paper by Robalewski[36] on the "membrane balloon" effect in osmometry; the previously mentioned paper by Brzeziński[20] on the determination of the second virial coefficient and the molecular weight of an isotactic fraction of polypentene; a paper by Skwarski[37] on the osmometric determination of the molecular weights of *N*-substituted polyamides; and papers by Kalfus[38] on the errors in osmometric measurements, and modifications to apparatus preventing the membrane balloon effect.

Cryoscopy is now generally accepted as a convenient method for determining very low molecular weights[39-42] and those of polymers which have not been thoroughly studied.

Other methods for the quantitative determination of the molecular weight of polymers are for the most part modifications of chemical methods of determination from terminal groups[43,44], for example using tracer atoms or electrochemistry.

There are other noteworthy papers describing new techniques. These include a paper by Kryszewski[45], demonstrating the possibility of calculating the constants of the viscometric equation from the results of X-ray diffraction studies, and a paper by Łabudzińska[46] describing the construction of a simple apparatus of her own design, which makes it possible to determine the molecular weight and the second virial coefficient with sufficient accuracy from light scattering measurements. The method was tested using polystyrene solutions.

In general terms, we can say that none of the Polish research centres have carried out systematic studies on the determination of molecular weights as the main aim of their research work. Most of the papers cited deal with developments following from earlier work, for example on the kinetics of polymerisation processes or the study of the dependence of the properties of polymers on their molecular weight.

This approach is revealed in the nature of papers in this field. Polish authors have first of all developed measurement procedures, or introduced simplifying modifications, or have found systems and corresponding constants for studying a large number of interesting materials for which insufficient published data were available.

The situation is quite different when we come to the characterisation of polydispersity. Although in this field also studies involving the investigation of reaction mechanisms and other work on kinetics are being carried out, there is a large number of papers devoted exclusively to methods of fractionation and methods of determining molecular weight distribution functions.

Of the analytical methods characterising polydispersity, only two have aroused great interest: sedimentation analysis and turbidimetric titration. As already noted, only one research centre — The Scientific Research Institute of the "Oświęcim" Chemical Plant — has examined the use of the ultracentrifuge for the fractionation of polymers.

Of the papers which have been published there, two deal with the determination of the molecular weight distribution function for butadiene-styrene rubber (Kalfus and coworkers[47]) and stereoregular polybutadiene (Mitoraj[48,49]). The authors discuss the influence of the polymerisation parameters on the distribution function, and also the influence of the distribution function on the physicomechanical properties.

Analogous papers deal with the relationship between polymerisation parameters and the results of sedimentation analysis for polystyrene[50] and with extensive studies of the relationship between the polydispersity and properties of rubber[51].

All these papers are clearly experimental in character; a more theoretical approach is adopted in two papers by Kalfus[52,53], in which, contrary to the views of Schulz and Horbach, he puts forward a simplified method for evaluating the results of sedimentation analysis, involving standardisation and calibration.

Finally, one paper[54] has been devoted to purely methodological problems. The authors suggest the use of a preparative centrifuge for the fractionation of polymers. After centrifuging, the specimens are frozen and separated into fractions mechanically.

Again only one research centre in Poland — The Synthetic Materials Institute — has examined the use of turbidimetric titration to characterise polydispersity. This subject is discussed in several papers by Krozer and coworkers[55-57]. The authors, who used these methods to characterise polycarbonates, state that the degree of dispersion of the precipitate obtained is independent of mole-

cular weight, so that the turbidimetric curves obtained can be used to characterise the polydispersity. These methods are also being applied to other materials to permit comparison with results obtained by other methods.

Polish authors have shown much greater interest in methods for the preparative determination of polydispersity; there are a fairly large number of papers dealing with fractionation, and this work is being carried out in various research institutes. Considerable attention is being paid to fractionation by the separation of two liquid phases.

Here, mention must be made of work by Basiński and coworkers[58-60] on the fractionation of various vegetable tanning agents by the separation of two liquid phases in systems with mixed solvents.

In the Physical Chemistry of Polymers Faculty of Lodz Polytechnical Institute, the method involving the separation of two liquid phases is used for the fractionation of synthetic polymers which crystallise particularly readily.

Two systems suitable for the fractionation of polyamides have been found[61-67]. The first is the phenol–ethylene glycol–water system, and the second, which is more suitable from the experimental viewpoint since the rate of separation of the layers is high, is the phenol–tetrachloroethane–n-heptane system. The latter system has also been used with good results for polyethylene terephthalate[68,69].

A similar method involving a slightly different procedure was used to study the fractionation of polycarbonates[70]. Although polycarbonates crystallise slowly and with difficulty from melts, they crystallise readily from solution. For this reason, separation into liquid fractions is important. The authors chose the dioxan–n-heptane system, in which equilibrium is first established between the liquid phases, after which a precipitate forms. The fractionation of polycarbonates with the formation of solid precipitates was studied by Brzeziński and Wajnryb[71] using the chloroform–petroleum ether system.

A combined extraction–precipitation method is now being used in the Physical Chemistry of Polymers Faculty to characterise low-molecular-weight epoxy-resins[72].

The fractionation of poly(vinyl chloride) in the cyclohexanone–glycol system was studied by Ulińska and coworkers[73].

A group of papers has been devoted to the fractional dissolution procedure.

Fractionation involving the extraction of fine fibres of viscose rayon was studied by Skwarski[74]. The use of extraction in a fractionating column has been developed for several materials. Polyethylene has been fractionated in a Francis column at elevated temperature in the xylene–Cellosolve system using graphite as carrier[75].

The column method has also been used for the fractionation of polycarbonates[76], the results obtained being similar to those obtained by precipitation.

Pentone has been fractionated by extraction in a column at elevated temperature (117°) in the cyclohexanone–diethylene glycol system using sand as carrier[77].

A number of papers have been devoted to total fractionation. This method was developed for poly(vinyl alcohol) using the acetone–water system[78].

One joint experimental–theoretical paper[79] and one purely theoretical paper[80] have been devoted to studies of the selectivity of the method.

In addition, there are a large number of papers which deal with the problems of fractionation only indirectly. Some of these papers deserve special mention.

Sibiński and Gralewicz[81] studied the change in polydispersity taking place during the pre-ripening of alkali cellulose. The work is of technical importance, the material studied being cord cellulose.

Turska and Skwarski[82-84] studied chiefly the changes in the polydispersity of polyethylene terephthalate during polycondensation and thermal degradation. They confirmed that during polycondensation, with change in the degree of completion of the reaction, the distribution function changes in accordance with Flory's theory, whereas during thermal degradation it leads to products with greater molecular uniformity; the function obtained corresponds more closely to the theory of Korshak and Slonimskii. The changes in the polydispersity of polyethylene terephthalate under the influence of irradiation have also been studied[85]; the distribution found corresponds most closely to Flory's ideas. An analogous result was obtained in the heat treatment of stabilised polyamides[86].

A joint paper[87] was devoted to the dependence of the mechanical properties of butadiene–styrene rubber on the molecular weight distribution function. It was found that a relationship exists between the polydispersity of the specimens studied and the maximal elasticity, tensile strength, and other mechanical parameters. The influence of the conditions of the polymerisation of styrene on the molecular weight distribution was studied by Kalfus and coworkers[88]. Kamińska[89] carried out analogous studies for polyvinyl chloride.

In many papers on kinetics, which in view of their specialised subject matter will not be discussed here, the distribution functions were determined in order to characterise the product completely.

Summarising these problems related to the fractionation of polymer solutions, it may be concluded that the work carried out in Poland in this field is predominantly experimental in character. An undoubted achievement is the large number of new systems which have been developed and verified. It is worth emphasising that the new fractionation systems have considerable advantages from the practical viewpoint, since they generally reduce considerably the duration of the fractionation with an appreciable saving of time.

In addition to papers dealing with methods for characterising polydispersity, there are also in this field a fairly large number of studies of another type, devoted to an analysis of the changes taking place during the formation of polymers, and also on the determination of the dependence of the physicomechanical properties of polymers on the distribution function. Since it has been established many times that there is a close relationship between the polydispersity of a polymer and the possibility of its practical application, and also since the polydispersity undergoes marked changes under the influence of various parameters of the polymerisation processes, the studies devoted to these problems are extremely interesting.

While taking account of the pure research aspect, which in this field makes it possible to obtain information on phenomena and relationships which have not been clear

until now, it is necessary to emphasise the practical importance of this field of study. A knowledge of the changes associated with polydispersity, which can take place during an industrial process, may give important information for the correction and control of this process. Control of the change in distribution functions of the product obtained or a re-treated product, even with rapid methods of study (with which difficulties are still associated) can hardly provide extensive possibilities in industry. On the other hand, it would undoubtedly be very useful from the industrial viewpoint to be able to control a process for the production or processing of polymers by altering the molecular weight distribution as desired. To achieve this, thorough development of the theoretical principles is obviously necessary. This is one of the reasons why I consider that the study of the relationship between polymerisation processes and the polydispersity and properties of macromolecular products is a very important field of research.

The very important relationship between work which at first sight concerns purely theoretical problems and work concerning industrial problems is also clearly shown in another field, which is represented fairly extensively in Poland; this work is described in theoretical papers and in a small number of experimental papers devoted to work carried out in the Technical Physics Laboratory of the General Chemistry Institute, on the hydrodynamics of polymer solutions. The authors, Ziabicki and Takserman-Krozer, have for a number of years been making a thorough study of a single problem, which has still not been solved. This problem concerns the behaviour of macromolecules in fields with other than transverse velocity gradients. As far as polymer solutions are concerned, the theory of their behaviour in the field of a transverse velocity gradient, like that for capillary viscometers, has for long been extensively treated in the scientific literature.

It should be noted, however, that there exist a number of important phenomena to which this theory cannot be applied, such as the formation of jets from the spinning solution in the production of synthetic fibres. The authors cited are therefore gradually beginning to develop a more general theory. The first papers in this field are purely theoretical[90-93] and begin with the simplest systems, that is a field with longitudinal velocity gradient and an immobile rigid ellipsoidal molecule. The first papers examine problems of the viscosity of a dilute solution and the orientation of this type of rigid molecule. The subsequent papers deal with the more complicated case of flexible macromolecules in solution and the viscosity of dilute solutions of these macromolecules in a field with longitudinal gradient.

The next stage, published jointly by both authors[94-99], expands previous discussions, but from a slightly different viewpoint. This series of papers is devoted to the problem of the restoration and breakdown of liquid fibres. Of these papers, only the last is confirmed experimentally by fast cinematography.

The earlier papers examine theoretically possible mechanisms for the restoration and breakdown of the jet under the influence of various parameters.

Subsequent papers by Takserman-Krozer[100-107] examine and summarise earlier studies of the properties of solutions of flexible chain macromolecules in the field of a general velocity gradient. On the basis of theoretical discussions, the author reaches general solutions characterising the distribution function, the orientation and deformation of the macromolecules, the time dependences, and other quantities.

Despite the fact that other work by these authors has not yet solved the problem raised, it can be confidently stated that an important step forward has been taken in this field.

These papers also provide an interesting example of work which is clearly theoretical in character but which should undoubtedly have a considerable influence on methods for organising the industrial process of fibre formation.

Another field which although not represented by a large number of papers has nevertheless aroused the interest of a number of authors is the study of polyelectrolyte solutions. Here mention may be made of the work of Ulińska, Wojtczak, Huppental, and others in the General Chemistry Faculty of the Copernicus University in Torun[108-116], devoted primarily to the study of various properties of polymethacrylic acid solutions, namely its adsorption, analytical methods for its determination, etc.

Bolewski[117] is studying polyelectrolyte solutions from another viewpoint; he is investigating the influence of the ionic strength of the solution on its properties.

Kryszewski[118,119], who is concerned chiefly with other problems, has also devoted two interesting papers to polyelectrolyte solutions. It can be seen that this field is attracting fairly serious attention from Polish authors working on polymers.

As already noted, the general character of research work in Poland, devoted to the study of polymer solutions, can be described as involving attempts to apply science in the national economy. Even papers which appear purely theoretical are generally of value as providing a theoretical basis for future industrial processes. This is as it should be.

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THE CHEMISTRY OF ALLENE DERIVATIVES

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I. INTRODUCTION

Research workers studying the chemistry of polyunsaturated compounds have recently been paying increasing attention to substances containing an allenic group in their molecule. This is not only because, from its chemical nature, the allenic double bond system is of great interest in the study of the reactivity of different types of polyunsaturated compounds. The interest is due in considerable measure to the fact that various types of functional derivatives containing this bond system, together with polyyne and diene groups, have been found among plant (including fungal) metabolites. Although the number of these natural compounds is still small, the very presence of such extremely unstable compounds among the products of the vital activity of cells is of great interest to biochemists. Furthermore, these types of compounds have been found to possess high antibacterial and fungicidal activity, which is to a considerable extent associated with the presence of an allene grouping.

Allenic systems are extremely unstable chemically, tending to undergo not only polymerisation and addition reactions but also ready acetylene–allene–diene conversions and various rearrangements. All this greatly hampers the synthesis and the chemical study of functional derivatives of the allene series, and makes it urgently necessary to work out convenient methods for the preparation of such polyunsaturated systems. Since great interest is being shown at the present time in various types of allenic compounds, and previous reviews[1-3] have discussed mainly allenic hydrocarbons, we consider that a literature survey of methods of synthesis and the reactivity of functional derivatives of allenic compounds will be of undoubted interest.

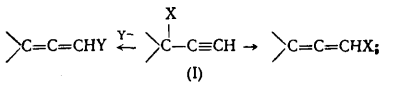
II. METHODS OF PREPARATION

The published information shows that functional derivatives of the allene series are obtained mainly by two methods. One of these is based on various types of acetylene–allene rearrangement of acetylenic systems, whereas 1,4-addition at a butenyne bond system underlies the second method.

1. Isomerisation of Acetylene Derivatives

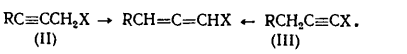
This general method of obtaining allene structures is based on two types of rearrangements characteristic of acetylene derivatives — (*a*) anionotropic rearrangement of

prop-2-ynyl systems of type (I) in the presence of catalysts or in the course of substitution reactions



(I)

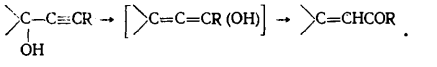
(*b*) prototropic isomerisation of prop-2-ynyl systems of types (II) and (III)



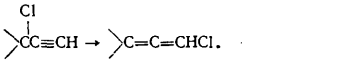
(II) (III)

Methods of synthesising functional derivatives of allene from the corresponding substituted derivatives of acetylene will be examined in this sequence.

(*a*) Anionotropic rearrangement of acetylenic alcohols and their derivatives. Rearrangement of an acetylenic to an allenic system is assumed to be an intermediate stage in the isomerisation, under the influence of acids, of acetylenic tertiary carbinols into unsaturated ketones (the Meyer–Schuster rearrangement)[4] and into $\alpha\beta$-unsaturated aldehydes (the Rupe rearrangement)[5]:

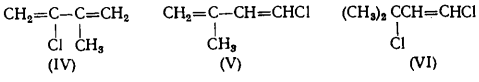


It has subsequently been shown that other acetylenic tertiary alcohols, including butenyne[6] and butadiyne[7] derivatives, are capable of analogous rearrangement. Among prop-2-ynyl derivatives, rearrangements of the chlorides of acetylenic tertiary alcohols have been studied the most thoroughly. Favorskaya and Favorskii[8] were the first to show that 3-chloro-3-methylbut-1-yne isomerises smoothly, under the influence of copper(I) chloride in ammonium chloride and concentrated hydrochloric acid, into 1-chloro-3-methylbuta-1,2-diene:



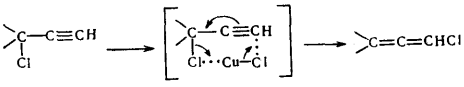
This method has been used to prepare several 1-chloroallene homologues[9–12], including the simplest 1-chloropropadiene[13], from various acetylenic alcohols.

It has subsequently been shown that such isomerisations do not yield unequivocal results: in the isomerisation of 3-chloro-3-methylbut-1-yne[9,14], for example, a mixture of products is formed, containing, together with the halogenoallene, such further isomerisation products as the chlorobutadienes (IV) and (V) and the dichloro-derivative (VI):

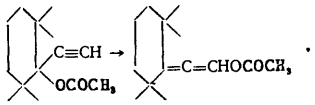


(IV) (V) (VI)

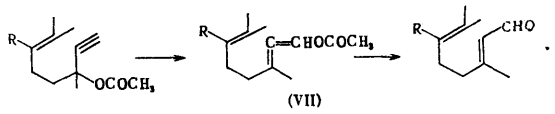
Considerably less work has been done on the rearrangement of acetylenic bromides[13,15–17]. The rearrangement of halogenoprop-2-ynyl systems to halogenoallenes represents a peculiar example of a 1,3-migration occurring by a mechanism of cyclic electron transfer[14]:



The isomerisation of acetates of acetylenic tertiary alcohols has also been described. The Landors[18], for example, observed the formation of an allenic acetate in up to 90% yield in the pyrolysis of 1-ethynyl-2,2,6,6-tetramethylcyclohexyl acetate:



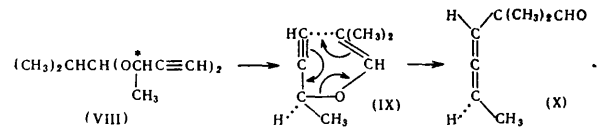
Recently Isler and his coworkers[19] have established that such acetates readily undergo rearrangement when heated in glacial acetic acid in the presence of copper powder or salts of copper or silver:



(VII)

Almost quantitative yields of unsaturated acetates of the type (VII) were obtained in this way. By means of this reaction it has been possible to work out an elegant method for the synthesis of various $\alpha\beta$-unsaturated aldehydes, including citral, farnesal, and phytal [3,7,11,15-tetramethylhexadec-2-enol].

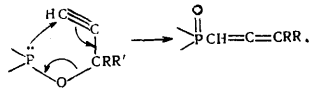
The synthesis has been described[20] of optically active 2,2-dimethylhexa-3,4-dienal (X) by the pyrolysis of dextrorotatory 2-methyl-3,3-bis-(1-methylprop-2-ynyloxy)propane (VIII). Formation of this product probably results from Claisen rearrangement of an intermediate 2-methylprop-1-enyl ether (IX) by a mechanism of cyclic transfer of electrons:



(VIII) (IX) (X)

It has recently been shown that, in the case of vinyl and chloroalkyl prop-2-ynyl ethers, the Claisen rearrangement is a general method for the synthesis of allenic aldehydes[21–23]. Allenic ketones are obtained in a similar manner, but they are very readily isomerised into conjugated dienones[24,25].

Detailed studies have recently been made of other interesting methods of synthesis, in which prop-2-ynyl esters are used for the preparation of allenes containing phosphorus. The prop-2-ynyl esters formed from acetylenic alcohols and halogen derivatives of tervalent phosphorus readily (in ether–pyridine at 20°) undergo intramolecular acetylene–allene rearrangement to give 75–100% yields of the allene derivatives. In view of the structure of the products, the rearrangement is explained by intramolecular migration in the five-centre intermediate system[26–28]:



Primary, secondary, and tertiary acetylenic alcohols can be successfully used in the above reactions[26–31]. Increasing the number of methyl substituents in the prop-2-ynyl portion not only increases the yield but also stabilises the allene derivatives, obviously owing to the inductive effect of the methyl groups, which prevent further prototropic isomerisation.

The rearrangement of prop-2-ynylammonium halides[32] under the influence of sodamide also results in allene derivatives. An interesting sequence of isomerisations into

allene and cumulene systems has been observed in amines containing a butenynyl group[33]:

$$(CH_3)_2CC{\equiv}CCH{=}CH_2 \rightarrow (CH_3)_2C{=}C{=}C{-}CH{=}CH_2 \rightarrow (CH_3)_2C{=}C{=}C{=}CHCH_2NR_2$$
(NR$_2$ at the first and second carbons)

It has repeatedly been observed that acetylene–allene isomerisation takes place during the occurrence of substitution reactions. Reaction of 3-chloro-3-methylalk-1-ynes with silver acetate in glacial acetic acid gives a mixture[34] of the allenic acetate (XI) and the normal acetylenic acetate (XII), the latter being the sole product when the reaction is conducted under the influence of potassium acetate:

$$R(H_3C)C{=}C{=}CHOCOCH_3 \xleftarrow{CH_3COOAg} R(H_3C)CCl{-}C{\equiv}CH \xrightarrow{CH_3COOK} R(H_3C)C(OCOCH_3){-}C{\equiv}CH.$$
(XI) (XII)

Silver propionate under similar conditions gave 3-methylbuta-1,2-dienyl propionate[35].

Prop-2-ynyl halides react with metal cyanides in the presence of copper(I) bromide at 60–120° to form allenic nitriles[36,37]. In the case of sterically hindered acetylenic tertiary bromides the yields reach 80%:

$$BrCRR'C{\equiv}CH \xrightarrow{Cu_2CN_2} RR'C{=}C{=}CHCN.$$

Interaction of 3-chloro-3-methylbut-1-yne with trialkyl phosphites at 130–150° results in moderate yields of dialkyl 3-methylbuta-1,2-dienylphosphonites[38]. Primary and secondary amines readily add on to prop-2-ynyl halides, merely forming acetylenic amines[39]. However, Hennion has recently reported[40,41] that, in the alkylation of certain sterically hindered prop-2-ynyl chlorides with tertiary amines, it has proved possible to obtain quaternary salts of allenylamines in 60–80% yields:

$$(CH_3)_2CC{\equiv}CH \xrightarrow{(CH_3)_3N} (CH_3)_2C{=}C{=}CH\overset{+}{N}(CH_3)_3\,\overline{Cl}.$$
(Cl at the propargylic carbon)

Not all tertiary amines react in this way, the type of reaction which occurs depending also on the basic strength and the nucleophilic character of the amine[41].

A general method for obtaining allenic acids (XIII) is based on the action of nickel carbonyl and hydrogen chloride on acetylenic alcohols[42–45], but the yields are usually low (10–20%):

$$RR'CC{\equiv}CH \xrightarrow[Ni(CO)_4]{HCl} RR'CC{\equiv}CH \xrightarrow[(R''OH)]{} RR'C{=}C{=}CHCO_2R''$$
(OH at the propargylic carbon; Cl at the propargylic carbon; (XIII))

where R = R′ = H, CH_3, C_2H_5; R = H, R′ = CH_3, C_3H_7, C_6H_5.

The reaction of prop-2-ynyl halides with acetylenic components (in particular with acetylenic alcohols) under the influence of copper salts in an amine medium provides an interesting route for the synthesis of acetylenic–allenic products (the yields reaching 80%)[46]:

$$R_2CC{\equiv}CH + HC{\equiv}CCH_2X \xrightarrow[NH_4OH]{Cu_2Cl_2} R_2CC{\equiv}CCH{=}C{=}CH_2$$
(OH at the propargylic carbon)

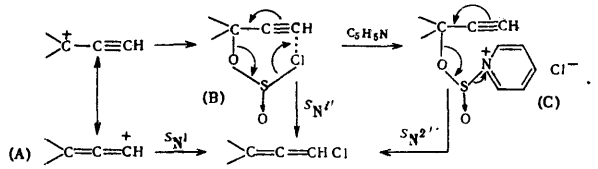
where X = Cl, Br, p-$CH_3C_6H_4SO_2$; R = H, CH_3, C_2H_5.

The isomerisation of acetylenic tertiary alcohols under the influence of concentrated hydrobromic acid in the presence of copper(I) bromide has recently been suggested as a method for the preparation of various 1-bromoallenes[47,48]:

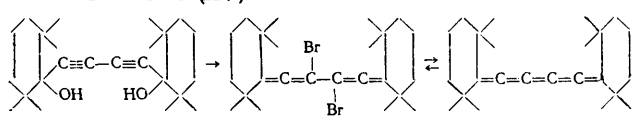
$$RR'CC{\equiv}CH \xrightarrow{HBr/Cu_2Br_2} RR'C{=}C{=}CHBr.$$
(OH at the propargylic carbon)

This method gives a high yield (60–80%) of quite pure bromoallenes (the content of acetylenic derivatives does not exceed 2–5%). An extremely important feature is that in this case the reaction proceeds stereospecifically, and optically active 3,4,4-trimethylpent-1-yn-3-ol yields the optically active allenic bromide.

Jacobs[49,50] and Landor[51,52] used the reaction of acetylenic alcohols with thionyl chloride for the synthesis of chloroallenes. This reaction is conveniently conducted in dioxan medium, is accelerated by the addition of bases (pyridine), and from sterically hindered alcohols gives good yields (up to 75%) of chloroallenes. Acetylenic secondary alcohols give considerably lower yields, and the reaction is complicated by the formation of byproducts[50,53]. Both the above reactions are characterised by the absence of prop-2-ynyl halides as intermediate products, so that the formation of halogenoallenes is not a result of their anionotropic rearrangement. Furthemore, these reactions proceed stereospecifically, in spite of the disappearance of the centre of asymmetry present in the original acetylenic alcohol. It is hardly possible to explain these results on the assumption that the reaction involves intermediate formation of a carbonium ion (A). Formation of an optically active chloroallene could conceivably occur through a cyclic transition state (B) (by an S_Ni' mechanism). In that case, however, the reaction velocity should be independent of the catalytic action of bases. Nevertheless, in the absence of bases the reaction of acetylenic alcohols with thionyl chloride gives very low yields, even when sterically hindered alcohols are employed. This suggests an S_N2' mechanism, the role of pyridine probably consisting in formation of a pyridinium salt (C), in which the substitution takes place under the influence of chloride ions. Preservation of configuration can then be explained either by a double inversion or by formation of a rigid (undissociated) ion-pair[50]. In either case (S_N2' or S_Ni' mechanism) the chlorine should approach on the hydroxyl side of the alcohol. Thus the available data are not yet sufficient to settle unequivocally the problem of the reaction mechanism between acetylenic alcohols and thionyl chloride:



A few examples have been described of the formation of halogenated allenes by the reaction of acetylenic tertiary alcohols with phosphorus trichloride in pyridine[54] or with phosphorus tribromide[55,56]. By means of the latter reaction Bohlmann[55] obtained from the butadiynylene glycol (XIV), obviously as a result of a double prop-2-ynyl rearrangement, a 70% yield of a diallenic dibromide (XV), whose structure was established by conversion into the corresponding pentaene (XVI) and reconversion of the latter into the dibromide (XV):



(XIV) (XV) (XVI)

The corresponding allenic iodides are formed (mixed with acetylenic and 1,3-diene isomers) by the action of potassium or sodium iodide on the prop-2-ynyl halides[13,16,57,58] or

of hydriodic acid on acetylenic carbinols[59], but it is extremely difficult to isolate these iodides in the pure form owing to their great tendency to undergo polymerisation and rearrangement even on simple distillation. A practical method of synthesis consists in treating acetylenic alcohols with triphenylmethyl phosphite–iodine[60], the yields varying from 20% to 70%:

$$\underset{\underset{OH}{|}}{RCHC{\equiv}CH} \rightarrow RCH{=}C{=}CHI$$

where R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_5.

Another group of substitutions which yield allenic structures involve organometallic compounds (of magnesium, aluminium, and zinc) derived from prop-2-ynyl halides, which have been studied mainly by Prévost and his co-workers[61–63]. On the hypothesis that a free carbanion is formed[61], these workers consider that the MgBr derivatives result from attack by the electrophilic MgBr, so that the structure of the final product should depend on electronic and steric factors. In the case of prop-2-ynyl bromide (XVII, R = H) the carbanion will have the structure (XVIII), and since δ^- far exceeds δ'^- in this instance, the $^+$MgBr should attack the acetylenic carbon atom, which will yield the allenic system (XIX):

$$\underset{\underset{Br}{|}}{RCHC{\equiv}CH} \rightarrow \left[\overset{\delta'-}{R\overset{3}{C}H} \cdots \overset{2}{C} \overset{\delta-}{=} \overset{1}{CH}\right] \xrightarrow{\overset{+}{M}gBr} RCH{=}C{=}CHMgBr$$

(XVII) (XVIII) (XIX)

Similar relationships are observed with the bromides (XVII, R = CH_3); here steric hindrance at $C_{(3)}$ is also operative, which should result in the structure (XIX) exclusively. With the isomeric carbanion (XX), on the other hand, the steric factor will act in the opposite direction, and a mixture of acetylenic and allenic MgBr derivatives will be obtained:

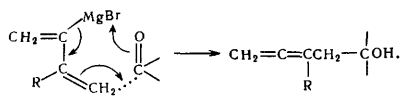
$$\underset{\underset{MgBr}{|}}{H_3CC{=}C{=}CH_2} \leftarrow \left[\overset{\delta-}{H_3CC} \cdots C \cdots \overset{\delta'-}{CH_2}\right] \rightarrow H_3CC{\equiv}CCH_2MgBr.$$

(XX)

In conformity with these views, it is only in the last case that formation of a mixture of acetylenic and allenic alcohols has been observed[61] on reaction with carbonyl compounds. In all other cases 2-acetylenic alcohols are formed exclusively. The formation of allenic together with acetylenic alcohols has been established in the reaction of prop-2-ynylzinc bromides with ketones[62–65] and in the Reformatskii condensation of prop-2-ynyl bromides with aliphatic and aromatic aldehydes[66–70]. Using condensation with acetone as example, however, it was demonstrated that allenic alcohols are formed, not as a result of reaction of the allenic ZnBr derivative with acetone, but from isomerisation of the acetylenic alcohol under the influence of the zinc salt[63,71]:

$$\underset{H_3C}{\overset{H_3C}{\diagdown}}\overset{OH}{\underset{|}{C}}CH_2C{\equiv}CH \rightarrow \underset{H_3C}{\overset{H_3C}{\diagdown}}\overset{OH}{\underset{|}{C}}{-}CH{=}C{=}CH_2 \xleftarrow{\overset{CH_3COCH_3}{X}} CH_2{=}C{=}CHZnBr.$$

An interesting case of the formation of allenic alcohols has been observed in the reaction of magnesium halide derivatives of diene bromides with carbonyl compounds, which probably occurs by a mechanism of cyclic transfer of electrons[72]:



Formation of an allene derivative has recently been noted in the addition of prop-2-ynyl-lithium to aliphatic aldimines[73] and also in the reaction of orthoformic ester with prop-2-ynyl-magnesium (or -zinc) halides[74,75].

The carboxylation of prop-2-ynylmagnesium halides with carbon dioxide or chloroformic ester has been known for a long time. Marvel[76] described the preparation of allenic acids from acetylenic tertiary chlorides. It was later established that this is a general type of reaction, Grignard reagents derived from prop-2-ynyl primary bromides being most readily carboxylated (in yields of 50–70%)[77–81]:

$$RC{\equiv}CCH_2Br \xrightarrow[2.\ CO_2]{1.\ Mg} RC{\equiv}CCH_2CO_2H + \underset{\underset{CO_2H}{|}}{RC{=}C{=}CH_2} \quad (XXI).$$

Although the reaction is complicated by formation of a dimeric allenic acid (see Section III, 2), in most cases the allenic acids (XXI) can be easily isolated in the pure form. Secondary and tertiary prop-2-ynylmagnesium halides show greater difficulty in reacting with carbon dioxide, but yield pure allenic acids of the type (XXII)[82]:

$$\underset{\underset{Br}{|}}{C_6H_5C{\equiv}CC(R)CH_3} \longrightarrow \underset{\underset{CO_2H}{|}}{C_6H_5C{=}C{=}C}\overset{R}{\underset{CH_3}{\diagup}}$$

(XXII)

where R = H, CH_3.

The condensation of dimethylbenzamide with certain substituted prop-2-ynylmagnesium bromides yields mixtures of acetylenic and allenic ketones[83]:

$$RC{\equiv}CCH(R')Br \xrightarrow[2.\ C_6H_5CON(CH_3)_2]{1.\ Mg} \underset{\underset{R}{|}}{C_6H_5COC{=}C{=}CHR'} + \underset{\underset{R'}{|}}{RC{\equiv}CCHCOC_6H_5}$$

(b) **Prototropic rearrangement of acetylenic systems.** Allene derivatives containing COOR, CN, CO, etc. groups have been obtained by the prototropic rearrangement of acetylenic compounds in the presence of bases under comparatively mild conditions. The isomerisation of acetylenic into allenic hydrocarbons is usually reversible[84], although the relative proportions of the acetylene–allene–diene products are greatly dependent on the structure of the initial acetylene, and perhaps on the conditions under which the rearrangement takes place. It might have been expected that the presence of electron-acceptor groups (CN, COOR, CHO, CO) in the allyl position relative to the acetylenic bond would not only facilitate prototropic rearrangement of acetylene to allene but also stabilise the cumulated system. In fact, the acetylenic epoxide (XXIII) readily isomerises under the influence of zinc oxide into the allenic aldehyde (XXIV)[85,86]:

$$RC{\equiv}C{-}\underset{\underset{CH_3}{|}}{C}\overset{O}{\diagup\diagdown}CH_2 \rightarrow RCH{=}C{=}\overset{CH_3}{\underset{|}{C}}CHO.$$

(XXIII) (XXIV)

The oxidation of 2-acetylenic secondary alcohols[67,72,87–90] with chromium trioxide in acetone and sulphuric acid is also accompanied by prototropic rearrangement, giving up to 70% yields of various allenic ketones. Allenic aldehydes and ketones can be obtained by the acid hydrolysis of butenynyl ethers of the type (XXV)[91–94]:

$$\underset{(XXV)}{R'C{\equiv}CCH{=}CR(OC_2H_5)} \rightarrow R'CH{=}C{=}CHCOR$$

where R = H, Alk.

Rearrangement has been observed also in the reaction of prop-2-ynyl halides with copper and potassium cyanides[95-97], by means of which several allenic nitriles have been synthesised in up to 50% yields:

$$RCH{=}C{=}CHCN \xleftarrow{KCN} RC{\equiv}CCH_2Br \xrightarrow{KCN} RC{\equiv}CCH_2CN.$$

The isomerisation of prop-2-ynyl sulphides in the presence of sodium ethoxide yields allenic sulphides[98-100]:

$$HC{\equiv}CCHR(SC_6H_5) \rightarrow H_2C{=}C{=}CR(SC_6H_5).$$

Arens has shown also that substituted 1-ethylthioalkynes (XXVI) on rapid treatment with an equivalent amount of sodamide are capable of giving a carbanion (XXVII), which on hydrolysis or alkylation gives up to 85% yields of the corresponding allenic sulphides[100-103]:

$$RCH_2C{\equiv}CSC_2H_5 \xrightarrow{(NaNH_2)} \underset{\text{(XXVII)}}{R\bar{C}HC{\equiv}CSC_2H_5 \leftrightarrow RCH{=}C{=}\bar{C}SC_2H_5} \begin{cases} \xrightarrow{H_2O} RCH{=}C{=}CHSC_2H_5 \\ \xrightarrow{R'Br} RCH{=}C{=}CR'SC_2H_5 \end{cases}$$

(XXVI)

Under the same conditions only the branched 2-acetylenic ethers (XXVIII) are converted into allenic ethers[99,104], the 1-acetylenic ethers merely forming 1,3-alkenynes:

$$\underset{\text{(XXVIII)}}{RR'CHC{\equiv}CCH_2OC_2H_5} \rightarrow RR'CHCH{=}C{=}CHOC_2H_5.$$

Prototropic rearrangement takes place very readily with $\beta\gamma$-acetylenic acids. Thus but-2(and 3)-ynoic acids are completely isomerised into the allenic acid when heated with 18% potassium carbonate solution to 40° [105] or by the action of sodamide in liquid ammonia[106]. However, 4-phenylbut-3-ynoic acid under the same conditions forms an equilibrium mixture with 4-phenylbut-2,3-dienoic acid in the proportions 2 : 3.[107] An equilibrium mixture (1 : 2) is obtained also by the isomerisation of 4-phenylbut-2--ynoic acid[108]:

$$C_6H_5C{\equiv}CCH_2CO_2H \rightleftarrows C_6H_5CH{=}C{=}CHCO_2H \rightleftarrows C_6H_5CH_2C{\equiv}CCO_2H.$$

The esters of these acids undergo rearrangement far more readily. The reaction is almost quantitative in the presence of potassium carbonate solution at 20°.[105] 4-Bromobuta-2,3-dienoic[109] and 2-chlorobuta-2,3-dienoic[110] esters also have easily been obtained in this way:

$$XC{\equiv}CCH_2CO_2R \rightarrow XCH{=}C{=}CHCO_2R$$

where X = H, Br.

The simplest pentynedioic acid (XXXI) does not exist, since, on preparation by oxidising the alcohol (XXX)† with chromium trioxide, it immediately undergoes prototropic isomerisation into penta-2,3-dienedioic acid[111]:

$$\underset{\text{(XXX)}}{HOCH_2CH_2C{\equiv}CCO_2H} \rightarrow [HO_2CCH_2C{\equiv}CCO_2H] \rightarrow \underset{\text{(XXXI)}}{HO_2CCH{=}C{=}CHCO_2H}.$$

It has been shown that an allenic system can be obtained only when its further isomerisation is difficult or altogether impossible. In this connection it is of interest to note the prototropic rearrangement of octa-3,5-diyne-1,8-dioic acid (XXXII), not into the diallenic acid (XXXIII), but into octa--2,4-dien-6-yne-1,8-dioic acid (XXXIV)[112]:

$$\underset{\text{(XXXIII)}}{HO_2CCH{=}C{=}CHCH{=}C{=}CHCO_2H} \xleftarrow{\chi} \underset{\text{(XXXII)}}{HO_2CCH_2(C{\equiv}C)_2CH_2CO_2H} \rightarrow \underset{\text{(XXXIV)}}{HO_2C[CH{=}CH]_2C{\equiv}CCO_2H}.$$

† A formula corresponding to (XXIX) does not appear in the Russian text (Ed. of Translation).

Prototropic rearrangement accompanied by migration of the double bond has been observed[66] in the alkaline saponification of the esters (XXXV), but the allenic acids (XXXVI) could not be isolated in the pure form:

$$\underset{\text{(XXXV)}}{RC{\equiv}CCH{=}CHCH_2CO_2CH_3} \rightarrow \underset{\text{(XXXVI)}}{RCH{=}C{=}CHCH{=}CHCO_2CH_3}.$$

Certain hydroxy-compounds, containing a double bond and a triple bond separated by a methylene group, also rearrange into allenic alcohols when boiled with solutions of bases[72,113-115] or with aluminium oxide[115-117]:

$$\gtrless C(OH)-C{\equiv}CCH_2CH{=}CH-R \rightarrow \gtrless C(OH)-CH{=}C{=}CHCH{=}CH-R.$$

2. Addition to Butenyne Systems

The addition of various reactants to a butenyne bond system constitutes a general method for the preparation of allenes. However, in several cases involving the addition of alcohols, halogens, and hydrogen halides, this method is greatly restricted by the difficulty of separating the mixture of acetylenic, allene, and conjugated diene derivatives which is usually formed. Separation may be achieved by careful fractional distillation, in which high temperatures must be avoided as they might cause interconversion of the isomers. On the other hand, such reactions as the reduction of butenyne derivatives and the addition of amines and halide esters usually proceed quite unambiguously, representing convenient and frequently the only possible methods for the synthesis of allene compounds containing these groups in the middle of the chain.

Addition of alcohols. This takes place in the presence of alkoxides: hexa-1,5-dien-3-yne reacts with methanol to give 3-methoxyhexa-1,3,4-triene[118]:

$$H_2C{=}CHC{\equiv}CCH{=}CH_2 \rightarrow H_3CCH{=}C{=}\underset{|}{\overset{OCH_3}{C}}CH{=}CH_2.$$

In the case of butenyne the allenic product formed initially is converted at ordinary pressure by allene–diene isomerisation into a 1-alkoxybuta-1,3-diene, and under pressure by allene–acetylene rearrangement into an acetylenic ether[119]:

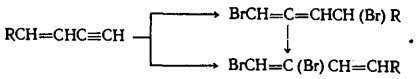
$$HC{\equiv}CCH{=}CH_2 \xrightarrow{CH_3OH} CH_2{=}C{=}CHCH_2OCH_3 \begin{cases} \rightarrow CH_2{=}CHCH{=}CHOCH_3 \\ \rightarrow CH_3C{\equiv}CCH_2OCH_3 \end{cases}.$$

Addition of thiols. In the presence of bases, thiols add to butenyne hydrocarbons mainly at the triple bond[120-122]: allenic sulphides are formed in insignificant quantity, and only in the case of butenyne itself has it been possible to isolate 4-alkylthiobuta-1,2-dienes[120,122]. The addition of thiols under radical conditions also results in partial formation of allenic sulphides[123]:

$$HC{\equiv}CCH{=}CH_2 \xrightarrow{RSH} \begin{cases} \rightarrow H_2C{=}CHCH{=}CHSR \\ \rightarrow H_2C{=}C{=}CHCH_2SR \end{cases}.$$

Addition of halogens. Only the bromination of butenyne and of alkenylacetylenes is of great practical interest[124,125]. In chloroform and at low temperatures butenyne is readily brominated to give a good yield of a

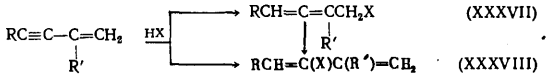
mixture of dibromides in which the allene and diene isomers predominate; with decrease in temperature the relative yield of the allenic dibromide increases:



It is possible that the diene dibromide is formed by allyl isomerisation of the allenic dibromide, which usually takes place very readily.

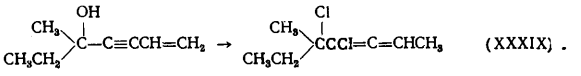
1,4-Addition predominates in the case of silicon-containing alkenynes [126]. The formation of halogenated allenes in small amounts has been noted also in the chlorination, chloroiodination, and halogenoarylation of butenyne and its homologues [119].

Addition of hydrogen halides. In the absence of catalysts, hydrogen chloride and hydrogen bromide add to butenyne [127-129] and its homologues [16,130-135] predominantly in the 1,4-positions to form the corresponding allene derivatives (XXXVII):

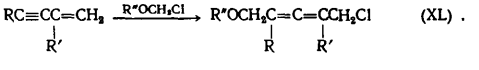


Some formation of halogenated dienes (XXXVIII) also occurs, either as a result of addition at the triple bond or by isomerisation of the halogenated allenes (XXXVII), the latter reaction taking place especially readily in the presence of copper salts (Cu_2Cl_2, Cu_2Br_2). Addition of hydrogen halides in the presence of these catalysts yields only the compounds (XXXVIII) [119]. When butenyne is hydrochlorinated in the presence of aluminium or zinc chloride instead of copper(I) chloride, the chief product is 4-chlorobuta-1,2-diene [129].

Nazarov and his coworkers [6] have established that but-3-en-1-ynylmethanols also add hydrogen halides, the 1,4-addition being preceded by replacement of the hydroxyl by halogen. The resulting allenic dihalide undergoes spontaneous isomerisation to the final conjugated diene products. Vartanyan [136] has recently succeeded in isolating (in 32% yield) the allenic dichloride (XXXIX) by the low-temperature hydrochlorination of 3-methylhept-6-en-4-yn-3-ol (at 18–20°):

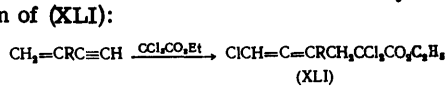


Addition of chloromethyl ethers. In the presence of bismuth trichloride as catalyst, addition to butenyne [137,138], hept-1-en-3-yne [139], 2-methylbutenyne [140], and hepta-1,6-dien-3-yne [141] takes place predominantly in the 1,4-positions to form chlorinated allenic ethers (XL):

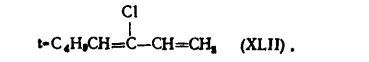


2,3-Dichlorotetrahydrofuran reacts in similar fashion with butenyne [142].

Ethers of secondary and primary alcohols derived from butenyne have recently been studied in this reaction [143]. It is interesting that allenic products are formed also in the reaction of t-alkyl halides with alk-1-en-3-ynes [144] in the presence of zinc chloride, the radical adding on to the double bond to give $C_2H_5CCl{:}C{:}CHCH_2C(CH_3)_3$. The reaction goes in the same direction (alkyl at the double bond) in the addition of trichloroacetic ester to alkenynes [145] with formation of (XLI):

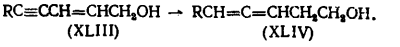


where R = H, CH_3. In contrast to this, addition of t-butyl chloride to butenyne takes place only at the triple bond, with formation of a halogenated diene (XLII) [119]:

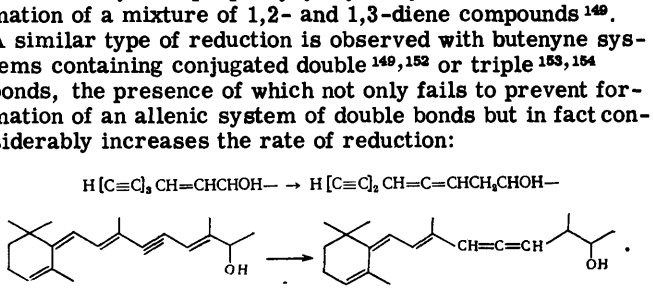


Addition of hydrogen. 1,4-Addition of hydrogen to but-3-en-1-ynylmethanols, with formation of the corresponding allenic alcohols as side-products, has been observed during cathodic reduction [146] and during hydrogenation with coppered zinc dust [147]. However, these reactions have not yet been used successfully for the preparation of allenes.

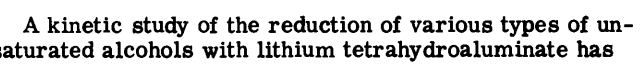
In 1954 Jones and his coworkers [148] studied the reduction of butenyne systems with lithium tetrahydroaluminate. Under these conditions alcohols of the type (XLIII) are selectively reduced (as a result of 1,4-addition) to give good yields of penta-3,4-dien-1-ol derivatives (XLIV) [149-152]:



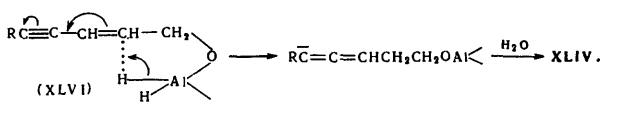
Further investigation of this reaction established that the presence of an allyl hydroxyl is a necessary condition for reduction to an allenic system. The simultaneous presence of allyl and prop-2-ynyl hydroxyls leads to the formation of a mixture of 1,2- and 1,3-diene compounds [149]. A similar type of reduction is observed with butenyne systems containing conjugated double [149,152] or triple [153,154] bonds, the presence of which not only fails to prevent formation of an allenic system of double bonds but in fact considerably increases the rate of reduction:



However, the compound (XLV) could not be reduced in this way [154]:

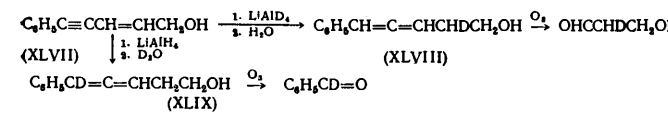


A kinetic study of the reduction of various types of unsaturated alcohols with lithium tetrahydroaluminate has shown [155] that nucleophilic addition of a hydride ion is the rate-determining stage in this reaction. In conformity with this, the mechanism of the reduction of pentenynol derivatives (XLVI) to allenes (XLIV) can be represented by the scheme

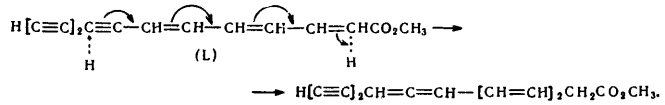


Results confirming the correctness of this mechanism have been obtained in a study of the reduction of 5-phenylpent-2-en-4-yn-1-ol (XLVII) with lithium tetrahydroaluminate and its deuterium analogue followed by decomposition with heavy and ordinary water respectively. The scheme below shows that only with the above reaction mechanism

can deuterated allenes (XLVIII) and (XLIX) be formed, the position of the deuterium in these compounds being proved by ozonisation to the corresponding monodeuterated aldehydes [155]:

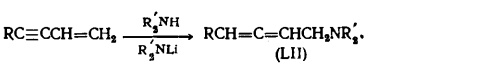


An unusual and extremely simple method of synthesising allenes, suggested by Bohlmann [154], is based on the reduction of alkenyne systems with aluminium amalgam in moist ether by Kuhn's method. Addition of hydrogen to the compound (L) takes place in positions 2 and 9, to give a very good yield of *trans-trans*-mycomycin (LI):

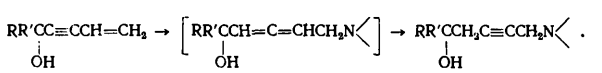


This new method of synthesising allenic structures evidently shows great promise for the preparation of complex natural allenes, and will undoubtedly find wide application.

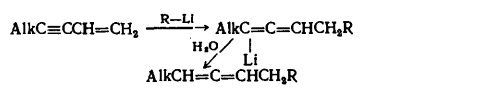
Addition of primary and secondary amines. Addition of these compounds to butenyne usually takes place on heating in an autoclave at 100°, and is a promising method for the preparation of allenic amines (LII, R = H) [156]:



The same reaction has found application in the synthesis of allenic diamines (LII, R = $CH_2N<$) [157]. Alcohols containing the butenyne system and hexa-1,5-dien-3-yne hydrocarbons [157] readily add amines in the 1,4-positions, but, under the reaction conditions with excess of amine present, the resulting allenic amino-alcohols are readily isomerised to acetylenic derivatives:

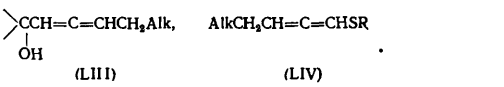


Addition of organolithium compounds. Petrov and Kormer [158] suggested a simple and general route for the preparation of allenes, based on the interaction of alk-1-en-3-ynes with organolithium compounds. This reaction involves an intermediate stage in which an allenyl--lithium is formed (with lengthening of the chain), hydrolysis of which gives good yields of allenic derivatives [159-162]:

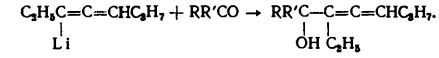


where R = Alk, Ar, pyrid-2-yl, R'_2P, R'_2N, etc.

Addition of lithium alkyls to butenyne alcohols [163] and to alkylthiobutenynes [164] yields allenic alcohols (LIII) and sulphides (LIV) respectively.

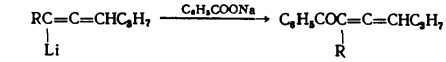


In the case of chlorides and ethers containing a butenyne system the course of the reaction with lithium alkyls is more complicated, a mixture of allenes and cumulenes being obtained [165]. In the above reactions lithium derivatives of allenes are obtained as intermediate products, which opens up wide possibilities for the synthesis of various allenic compounds. Several reactions of 1-ethylhexa-1,2-dienyl-lithium have so far been studied. Its condensation with formaldehyde, oxiran, and many carbonyl compounds, both saturated and unsaturated, has led to the synthesis of a large number of allenic alcohols [166-168]:



It is very significant that addition of allenyl-lithium at the multiple bonds in the starting materials was not observed.

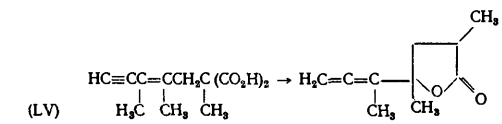
The allenic structure of the initial allenyl-lithium is preserved also during carboxylation [169], addition of pyridine and benzonitrile, and reaction with sodium benzoate [170]:



where R = CH_3, C_2H_5.

Alkenynyl-silicon and -germanium compounds on addition of lithium alkyls [171-174] and dialkyl-lithamides [175] yield mixtures of difficultly separable allenic and acetylenic products.

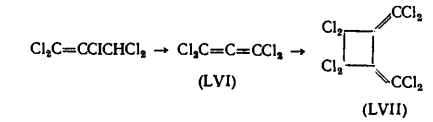
Other instances are known in which allenic derivatives are formed as a result of addition to butenynes. Among them are the reactions of butenyne amines with carbon disulphide [176], and also the formation of allenic lactones by the decarboxylation of malonic acids of the type (LV) [177,178]:



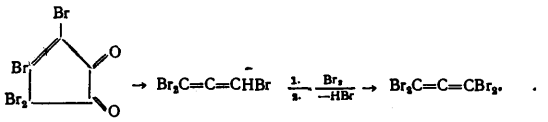
3. Other Methods

Dehydrohalogenation and pyrolysis are widely used for the preparation of polyhalogenated allenes. Blomquist [179] obtained 1,1-difluoroallene from ethylene and dibromodifluoromethane by a series of successive dehydrobrominations and brominations. This product has also been obtained by the pyrolysis of 1,1,2,2-tetrafluoro-3-methylenecyclobutane and of 2,2,3,3-tetrafluorocyclobutylidenemethyl acetate [180].

Dehydrohalogenation of the corresponding halogenated hydrocarbons by means of powdered or alcoholic potassium hydroxide or of sodamide has been used to obtain perfluoroallene [181], halogenoarylallenes [182,183], 4,4,4-trifluorobuta--1,2-diene [184], and alkoxyarylallenes [185-189]. The extremely reactive perchloroallene (LVI), which usually exists in dimeric form (LVII) [190,191], was obtained by Roedig [192] by the dehydrochlorination of pentachloropropene with sodamide in liquid ammonia:



This worker has recently succeeded in obtaining tri- and tetra-bromoallenes [193] by the reactions



Arens [194,195] noted the formation of considerable quantities of allenyl ethers when the *cis*-forms of β-halogenoalkenyl ethers were subjected to prolonged heating with caustic potash. A more unequivocal result is obtained with allenic systems in which the structure is fixed [196-198]:

$$CH_3{=}CBrCH_2CN \rightarrow CH_2{=}C{=}CHCN\ (CO_2CH_3).$$

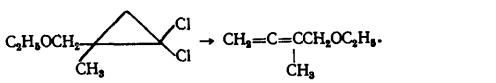
Isolated examples have been reported of the preparation of functional derivatives of allenes by the dehydration of alcohols [199] and the cleavage of acetals [200], nitro-derivatives [201], triglycerides [202], and derivatives of cyclobutane [203] and cyclopropane [204].

The reaction of but-2-ene-1,4-disulphonyl dichloride with ammonia and primary amines is accompanied by the evolution of hydrogen chloride and sulphur dioxide with the formation of allenic monosulphonamides [205]:

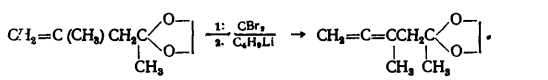
$$ClSO_2CH_2CX{=}CHCH_2SO_2Cl \xrightarrow{RNH_2} CH_2{=}C{=}CXCH_2SO_2NHR$$

where X = H, Cl, CH_3.

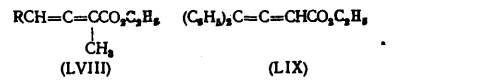
The cleavage of *gem*-dihalogenocyclopropane derivatives with lithium alkyls in ethereal solution provides a simple and convenient method of obtaining certain allenic ethers [206,207]:



The successive action of dibromocarbene and butyl-lithium on unsaturated alcohols [208] or 2-substituted dioxolan derivatives [209] yields the corresponding allenic alcohols and acetals in 15-85% yield:



The Wittig reaction has recently found application for the synthesis of 1,2-dienes. It has been used to obtain, from acid chlorides [210] (or ketens) [211] and the appropriate phosphoranes, allenic esters of types (LVIII) and (LIX) respectively.

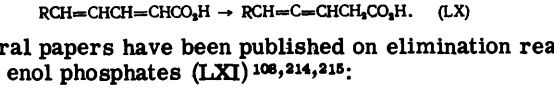


(LVIII) (LIX)

Optically active allene-1-carboxylic acids have recently been prepared in this way [212]. Alka-3,4-dienoic acids (LX, R = H, CH_3) are formed on ultraviolet irradiation of the alka-2,4-dienoic acids [213], but the yields are low:

$$RCH{=}CHCH{=}CHCO_2H \rightarrow RCH{=}C{=}CHCH_2CO_2H. \quad (LX)$$

Several papers have been published on elimination reactions of enol phosphates (LXI) [108,214,215]:



(LXI) (LXII) (LXIII)

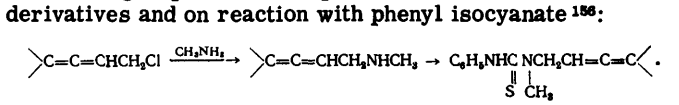
These reactions take place under comparatively mild alkaline conditions (at 25°), and simulate the biogenetic path for the synthesis of acetylenes in Nature [108,215]. Cymerman-Craig and Moyle [108] have shown that, in the presence of activating groups (C_6H_5, COOH), enol phosphates (LXI) are extremely readily converted into allenic compounds. The normal acetylenic products (LXII) formed at the same time may isomerise with (LXIII) under less basic conditions than are required for formation of the acetylenic group. The elimination of enol phosphates may, perhaps, be regarded as a chemical model of the biogenetic route for the formation of allenes in Nature.

III. CHEMICAL PROPERTIES AND REACTIONS OF FUNCTIONAL DERIVATIVES OF ALLENES

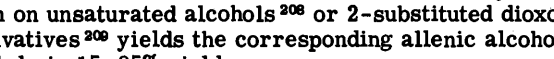
In conformity with the structure of allene [216,217], its functional derivatives are characterised by three types of chemical reactions — (1) reactions of the functional groups, not involving the allenic system, (2) additions at the allenic bonds, and (3) reactions involving isomerisation of the allenic system.

1. Reactions Not Involving the Allene Bond System

In halogenated allenic derivatives the halogen is extremely mobile, and can undergo various substitutions under the influence of neutral or weakly basic reagents (sodium carbonate, sodium acetate, potassium bromide, potassium iodide) [129,139,143,218]. Thus the action of amines on 4-chlorobuta-1,2-dienes has given various allenic amines [138,139-143,156], the allene group in which is preserved on formation of the derivatives and on reaction with phenyl isocyanate [156]:

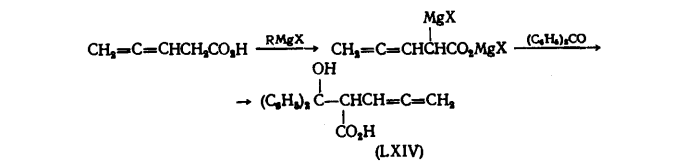


4-Chlorobuta-1,2-diene undergoes substitution with benzylmagnesium and especially phenylmagnesium bromide, to give allenic hydrocarbons [219]:



With other organomagnesium compounds [219-221] and with magnesium [222], however, only conjugated dienes are formed.

Penta-3,4-dienoic acid reacts with organomagnesium compounds to form a dimagnesium derivative, which with benzophenone yields an allenic product (LXIV) [223]:



(LXIV)

The reduction of 1-halogenoallenes with a zinc-copper couple in alcohol proceeds without affecting the double bonds [224], and provides a general method for the synthesis of allenic hydrocarbons [1]. Roedig [182] succeeded in reducing 1,1-dichloro-3,3-bischlorophenylallene by means of zinc dust in pyridine and glacial acetic acid:

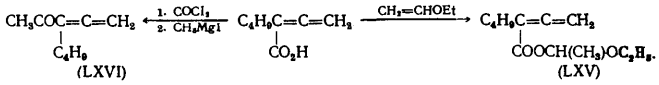
$$(ClC_6H_4)_2C{=}C{=}CCl_2 \rightarrow (ClC_6H_4)_2C{=}C{=}CH_2.$$

The allene group remains unaffected in the reduction of allenic ketones with lithium tetrahydroaluminate [89,90,93,225]. The oxidation of β-allenyl alcohols with chromium trioxide gives moderate yields of the corresponding acids [153,226,227]:

$$RC{\equiv}CCH{=}C{=}CHCH_2CH_2OH \rightarrow RC{\equiv}CCH{=}C{=}CHCH_2CO_2H.$$

2-Butylbuta-2,3-dienoic acid is stable to heating, and with excess of ethyl vinyl ether at 100° gives a quantitative

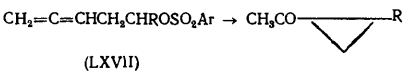
yield of the esterification product (LXV)[228]; the ketone (LXVI)[67] has been obtained by the action of methylmagnesium iodide on the chloride of this acid:



(LXVI) (LXV)

Allenic amides have also been obtained via the acid chlorides[43,78]. Kohler[229] prepared from 4-naphthyl-2,4-diphenylbuta-2,3-dienoyl chloride the corresponding carboxymethyl ester, which he separated into two optical enantiomers. In order to preserve the allene group in the original molecule, reactions must be conducted under mild and rigorously controlled conditions. However, side-reactions involving addition at the allenic bond system frequently occur[69,105,107].

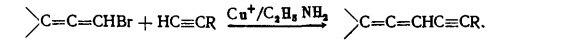
An interesting rearrangement into acetylcyclopropanes[225,230] has recently been observed in the hydrolysis of sulphonates of the type (LXVII):



(LXVII)

where R = H, CH_3.

The allenic system is preserved in the unsymmetrical condensation of 1-halogenoallenes[231] by the Chodkiewicz method:

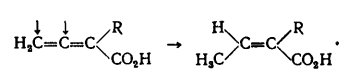


This is probably the most promising method for synthesising allenyne systems related to those occurring in Nature.

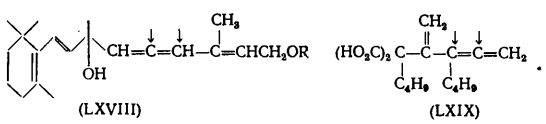
2. Addition Reactions

Reduction. The double bonds in allene readily undergo catalytic hydrogenation over platinum, palladium, or Raney nickel, with high yields of the resulting saturated products, and this method is widely used for the establishment of structure.

Incomplete hydrogenation of buta-2,3-dienoic acid in the presence of 1.5% of palladium on calcium carbonate gave *cis*-crotonic acid exclusively[105], i.e. the product resulting from addition of hydrogen at the $\beta\gamma$-double bond on the side opposite to the carboxyl:



The hydrogenation of 2-butylbuta-2,3-dienoic acid proceeds similarly[232], addition of hydrogen taking place at the less substituted double bond. Addition of hydrogen at one of the double bonds has been observed in the hydrogenation of the polyenol (LXVIII) in the presence of nickel[115], and also in the hydrogenation of the acid (LXIX) over platinum[233]:

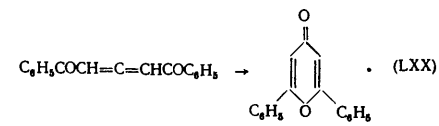


(LXVIII) (LXIX)

The reduction of 1-halogenoallenes with lithium tetrahydroaluminate shows very unusual features. Allenic chlorides[49] give mainly alkenes, alkanes, and small amounts of alkynes. In contrast to this, 1-bromo-3-methylbuta-1,2-diene[16] gives a 75% yield of a mixture of hydrocarbons comprising 61% of 3-methylbutyne, 36% of isopentane, and small quantities of alkenes. A more detailed study has been made of the reduction of 1-chloro-3-methylbuta-1,2-diene[234] with lithium tetrahydroaluminate, when two competitive reactions are involved — (*a*) replacement of chlorine by hydrogen (or deuterium), accompanied by complete allene–acetylene rearrangement, and (*b*) addition of the reagent at the allene double bonds, leading on subsequent hydrolysis to a mixture of the above hydrocarbons.

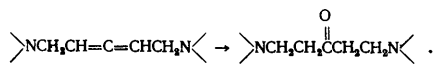
Addition of water, alcohols, thiols, and amines. Addition of these compounds, which is characteristic mainly of the acetylenic bond, takes place readily also with allenes. However, few examples of these reactions are known. 4-Chlorobuta-1,2-diene adds water in the presence of concentrated sulphuric acid[127], and allenic ketones are readily and quantitatively hydrated by dilute acids[72,90].

The action of 30% sulphuric acid on 1,5-diphenylpenta-2,3-diene-1,5-dione gave a 40% yield of the corresponding 4-pyrone (LXX), whose formation probably involves the initial addition of water[87,90]:



(LXX)

1,5-Bisdialkylaminopenta-2,3-dienes are hydrated when heated with mercury salts[157]:

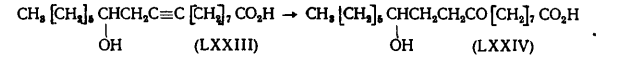


Allenic acids have been found to add water also in alkaline media[105,107]. Extraordinarily ready formation of the hydroxy-ketone (LXXII) was observed[69] on reduction of the sodium salt of the keto-acid (LXXI) with an alcoholic solution of potassium tetrahydroborate:



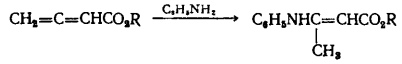
(LXXI) (LXXII)

It is interesting that hydration of the acetylenic acid (LXXIII) by mercury salts in sulphuric acid gives an isomeric hydroxy-keto-acid (LXXIV):



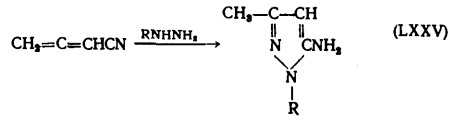
(LXXIII) (LXXIV)

Addition of alcohols and amines to allenes containing electronegative groups (CN, COOR, CO) takes place under considerably milder conditions than with acetylenic derivatives, the addition occurring at the unsubstituted double bond[105,235]. Brief treatment of buta-2,3-dienoic ester with aqueous–alcoholic caustic potash solution gives mainly β-ethoxycrotonic ester[105]. Piperidine and even aromatic amines add vigorously to an allenic ester even at room temperature, with formation of the corresponding β-substituted derivatives of crotonic ester[105]:



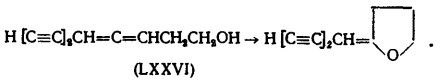
Alcohols, amines, and thiols add at the unsubstituted double bond also in buta-2,3-dienenitrile[97,236]. Addition of

substituted hydrazines is accompanied by ready cyclisation with the formation of an alkylated aminopyrazole (LXXV)[97]:



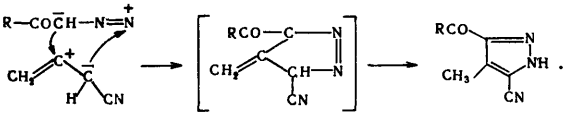
(LXXV)

Allenic ketones give quantitative yields of the corresponding pyrazoles and oxazoles on reaction with hydrazine hydrate[90,94,237] and hydroxylamine[72]. An interesting case of intramolecular addition has been observed with the butadiynylallenic alcohol (LXXVI)[153]:

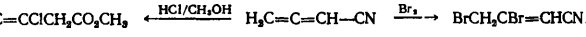


(LXXVI)

Such intramolecular additions may be of interest for the synthesis of various heterocyclic systems[90,97]. 1,3-Dipolar cycloadditions can also be used for this purpose. Success has recently been achieved in condensing buta-2,3--dienenitrile with various diazo-ketones[236] and obtaining the corresponding triazole and pyrazole derivatives:

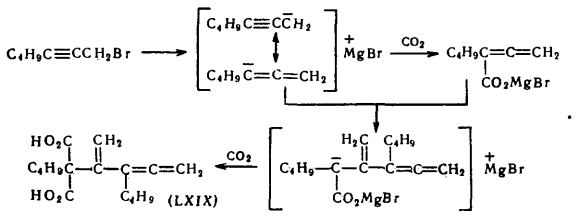


Addition of halogens and hydrogen halides. Addition to allenic compounds usually occurs very easily. Thus perchloroallene[192] and perfluoroallene[181] add two moles of chlorine even at -75°, and with 1,1-dichloro--3,3-di-*p*-chlorophenylallene[182] the reaction goes quantitatively at 20°. In the dark, however, perfluoroallene adds only one mole of chlorine and hydrogen halides[238]. On brominating 1,1-difluoroallene Blomquist[179] obtained a tetrabromide, but 1-chloro-5-ethoxy-4-methoxymethylenepenta-2,3-diene[143] and 1,1-dichloro-3,3-bischlorophenylallene[182] at 20° add bromine at only one double bond. Both the nitrile[97] and the ester[105] of buta-2,3-dienoic acid add only one molecule of bromine, at the unsubstituted double bond:



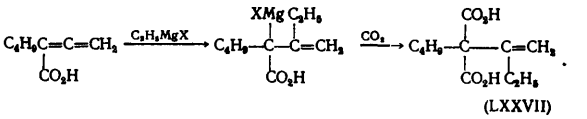
The addition of hydrochloric acid, however, takes place with the formation of $\beta\gamma$-unsaturated derivatives[97,105]. A similar type of addition has been observed also in the acid hydrolysis of the nitrile of octa-1,2-dienedicarboxylic acid[95].

The literature describes several examples of the addition of Grignard reagents at allenic double bonds. Mention has been made above[78] of the preparation of the allenic dicarboxylic acid (LXIX) by carboxylation of the organomagnesium derivative obtained from 1-bromohept-2-yne, the reaction probably being represented by the scheme[233]



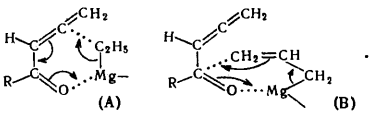
(LXIX)

It has also been shown[232,239] that the addition of organomagnesium compounds to 2-butylbuta-2,3-dienoic acid followed by carboxylation yields the unsaturated acid (LXXVII):



(LXXVII)

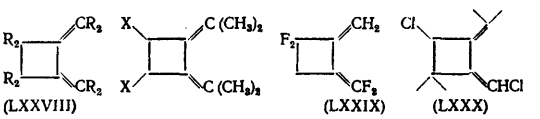
The structure of this acid (LXXVII) shows that the reaction results from addition at the $\alpha\beta$-double bond, not from 1,4-addition. Allenic ketones[72,89,90] with ethylmagnesium bromide also give products in which the ethyl group has been added at the allenic bond system, their formation probably involving a mechanism of cyclic transfer of electrons[72,240] (A):



(A) (B)

This mechanism may be supported by the formation of normal Grignard reaction products of allenic ketones with allyl and prop-2-ynyl halides, which is also interpreted by an electron-transfer scheme. Formation of a six--membered ring is preferable to an eight-membered ring for normal addition at the carbonyl group (B), which might have occurred in addition of allyl (prop-2-ynyl) at the allenic system. Such an explanation, however, is not the only possible one, and the direction of the reaction may also be subject to steric factors[241].

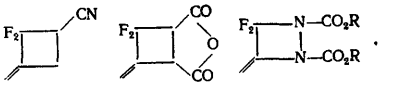
Thermal dimerisation. This is more characteristic of halogenated allenes than of allenic hydrocarbons[3]. The reaction usually occurs even at low temperatures, and results in four-membered dimethylenecycloalkanes[16,110,180-182,190-193,242], whose structure as 1,2:1,2-addition products (LXXVIII) has been established by means of their infrared and nuclear magnetic resonance spectra and their chemical reactions:



(LXXVIII) (LXXIX) (LXXX)

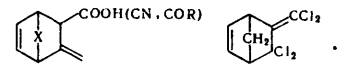
where R = Cl, Br, F and X = Cl, Br. It has recently been shown[56,243] that the dimerisation of 1-halogenoallenes may result in 1,2:2,3-addition products, (LXXIX) and (LXXX). Dimeric products are formed also under the influence of acidic reagents, such as acetic acid, thionyl chloride, and phosphorus tribromide[244,245].

Halogenated allenes can undergo cycloaddition as well as dimerisation. Reaction of 1,1-difluoroallene with acrylonitrile, maleic anhydride, and azoformic ester yields the corresponding four-membered adducts[180]



Wotiz[228] noted that 2-butylbuta-2,3-dienoic acid does not undergo the Diels–Alder reaction, either as a diene or as a dienophile. It was subsequently shown, however, that allenic derivatives can be used as dienophiles of an unusual kind. Buta-2,3-dienoic acid was found[246] to give with cyclopentadiene an adduct of the type (LXXXI). Analogous

products are formed by the condensation of the corresponding nitrile[97] and of allenic ketones[247] with cyclopentadiene, furan, and certain other dienes.



(LXXXI) X = O, CH_2 (LXXXII)

Roedig[192] has been able to effect the diene condensation of perchloroallene with cyclopentadiene (LXXXII) at -10°. The diene condensation of cyclopentadiene with optically active penta-2,3-dienedioic acid has recently been successfully employed[248] to establish the absolute configuration of the acid.

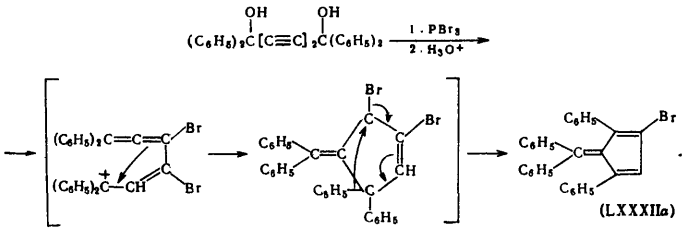
3. Isomerisation of Allenic Compounds

Isomerisation is a most characteristic feature of allenic derivatives. Under the influence of a solution of copper(I) chloride in concentrated hydrochloric acid, 1-halogenoallenes readily isomerise into conjugated 1-halogenobutadienes[8,9,14,64]. Jacobs and Petty[16] obtained a mixture of equal quantities of *cis*- and *trans*-1-bromo-3-methylbuta--1,3-dienes by the thermal isomerisation of 1-bromo-3--methylbuta-1,2-diene:

$$RCH_2CR'=C=CHX \rightarrow RCH=CR'CH=CHX.$$

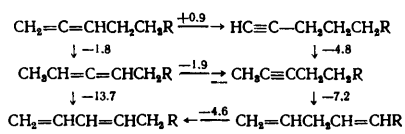
However, certain 1-halogenoallenes could not be isomerised under these conditions[10,136,157].

The interesting isomerisation has recently been described of tetraphenylhexa-2,4-diyne-1,6-diol in the presence of phosphorus tribromide in acetic acid[245], resulting in the fulvene (LXXXII*a*), this reaction undoubtedly involving intermediate allenic structures:



(LXXXII*a*)

Acetylene–allene isomerisations have already been mentioned above. Approximate heats of isomerisation (in kcal mole^{-1}) have been determined[249] for certain types of unsaturated compounds, which permitted these systems to be arranged as follows according to their tendency to interconversion



When discussing isomerisation in a series of functional derivatives of allene, however, we must bear in mind that the direction of isomerisation depends to a certain extent also on the nature of the functional groups. For example, allenic ethers[250] are in equilibrium with alkoxyacetylenic structures:

$$CH_2=C=CHOR \rightleftarrows CH_3C\equiv COR$$

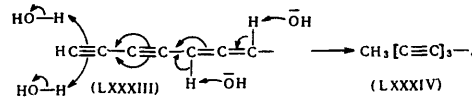
On the other hand, the isomerisation of derivatives of penta-2,3-diene-1,5-diol[139] and of allenic acids[105,227] yields only acetylenic compounds:

$$CH_3CH=C=CHCO_2H \rightarrow CH_3C\equiv CCH_2CO_2H.$$

The isomeric penta-3,4-dienoic acid[138] and other β-functional allenes[20,251] are converted under the same conditions into 2,4-diene derivatives:

$$CH_2=C=CHCH_2CO_2H \rightarrow CH_2=CHCH=CHCO_2H.$$

Allene–acetylene isomerisation plays an important part in establishing the structure of naturally occurring allene-polyynes. The mechanism of this rearrangement includes initial detachment of a proton by a strong base followed by its addition to another carbon atom of the molecule[84]. In the case of mycomycin[252,253] the rearrangement consists in migration of two protons and conversion of the allenediyne grouping (LXXXIII) into the corresponding alkatriyne derivative (LXXXIV):



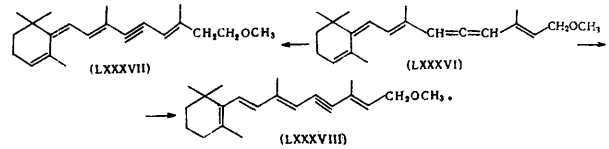
(LXXXIII) (LXXXIV)

However, the methyl ester of *trans*-mycomycin (LI) very readily underwent alkaline isomerisation with the formation of the tridecatetraenediynoic ester (LXXXV), whose structure was proved by an alternative synthesis[154]:

$$H[C\equiv C]_2{-}CH{=}C{=}CH[CH{=}CH]_2CH_2CO_2CH_3 \rightarrow H[C\equiv C]_2[CH{=}CH]_4CO_2CH_3.$$

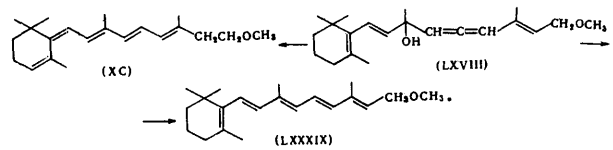
(LI) (LXXXV)

Interesting isomeric rearrangements have been observed with the allenic compound (LXXXVI)[115]. During chromatography on aluminium oxide it could already change into the acetylenic product (LXXXVII), and when boiled with alcoholic caustic soda it gave a mixture of (LXXXVII) and (LXXXVIII):



(LXXXVII) (LXXXVI) (LXXXVIII)

The polyenediol monomethyl ether (LXVIII) when boiled with lithium tetrahydroaluminate in ether isomerises into the methyl ether of vitamin A (LXXXIX), and on treatment with chromium acetate in strongly alkaline medium is converted into the *retro*-compound (XC)[115]:



(XC) (LXVIII) (LXXXIX)

Isomerisation of an allenic system is observed also in the abstraction of hydrogen halide from allenic chlorides[132,254] and dibromides[125,126], and also during the dehydration of allenic alcohols formed by the Reformatskii reaction[68-70]:

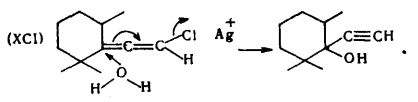
$$RCH_2CH=C=CHCH_2Cl \rightarrow RCH=CH{-}C\equiv CH \leftarrow \underset{\displaystyle OH}{RCHCH}=C=CH_2$$

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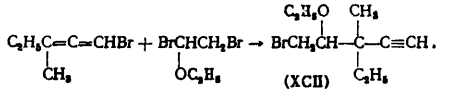
The cleavage of allenyl sulphides with sodamide[255], which gives 80–90% yields of a mixture of *cis*- and *trans*--isomers, may be of value for the preparation of substituted butenynes:

$$CH_3CH{=}C{=}C(R)SR' \xrightarrow{2\ equiv.\ NaNH_2} RCH{=}CH{-}C{\equiv}CH.$$

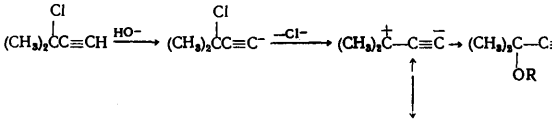
Substitutions in the halogenated allene series are often accompanied by isomerisation of the allenic system of double bonds. Although 1-chloro-3-methylbuta-1,2-diene does not react with silver acetate[34] and undergoes practically no solvolysis in 80% alcohol at 25°,[256] the allenyl chloride (XCI) is 90% converted into an acetylenic alcohol when heated with an alcoholic solution of silver nitrate[52]:



1-Bromo-3-methylbuta-1,2-diene reacts similarly with sodium iodide and with sodium phenyl sulphide, giving the corresponding acetylenic derivatives[16]. The action of ethoxy-1,2-dibromoethane on 1-bromo-3-methylpenta-1,2--diene also yields mainly acetylenic derivatives (XCII)[257]:

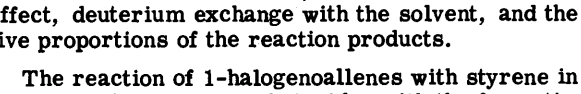


Interesting results have been obtained in a study of the solvolysis of 1-halogenoallenes. It has already been remarked above that 1-chloro-3-methylbuta-1,2-diene undergoes practically no solvolysis in 80% alcohol. In the presence of bases, however, the reaction is greatly accelerated, with the formation of 2-methylbut-3-yn-2-ol and its ethyl ether. A similar result is obtained with 3-chloro--3-methylbut-1-yne[256]. To explain these results, it was suggested that the rate-determining stage of the reaction was abstraction of a proton with formation of an intermediate carbene (XCIII):



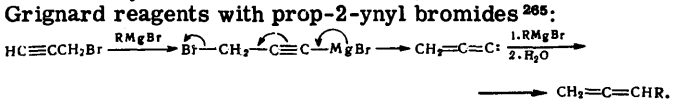
where R = H, C_2H_5. This mechanism of allene–acetylene rearrangement has found further support in the detailed work of Shiner and Wilson[17], who studied the kinetics, salt effect, deuterium exchange with the solvent, and the relative proportions of the reaction products.

The reaction of 1-halogenoallenes with styrene in the presence of potassium t-butoxide, with the formation of (XCIV)



where X = Cl, Br, also takes place by a carbene mechanism[258,259]. Alkynes of various structures[258,260–262] and dicarbene (:C=C=C:)[263,264] have also been used as starting materials in the above reaction with cyclohexene, isomeric butenes, and other alkenes.

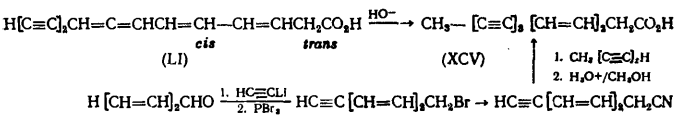
Formation of allenecarbene as an intermediate product has recently been observed in a study of the reaction of Grignard reagents with prop-2-ynyl bromides[265]:



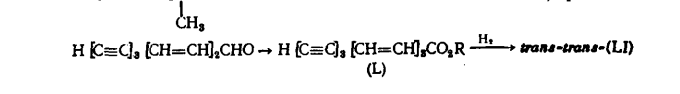
The accompanying formation of allenic hydrocarbons can best be explained by means of an intermediate allenecarbene.

IV. NATURALLY OCCURRING COMPOUNDS OF ALLENIC STRUCTURE

The number of compounds of this type is not yet large, but they constitute a very interesting group of optically active compounds exhibiting a broad spectrum of antimicrobial and fungicidal action. In chemical structure these compounds are polyunsaturated functional derivatives containing acetylenic, polyene, and allenic groups. The first representative of these substances was *mycomycin* (LI), which was isolated from the mould *Nocardia acidophylus* by Johnson and Burdon[266] in 1947. This antibiotic is very unstable in the crystalline state, and can be stored only in solution at -40°; it decomposes explosively at 75°. The structure of mycomycin was elucidated by Celmer and Solomons[252,267], who established that it contains an unbranched chain of carbon atoms with the empirical formula $C_{13}H_{10}O_2$. Absorption bands in the ultraviolet and infrared spectra[66,267] indicate the presence of diene and diyne groupings, unconjugated carboxyl, an allenic group, and ethynyl hydrogen. This together with other data has enabled mycomycin to be assigned the structure trideca--*trans*-3,*cis*-5,7,8-tetraene-10,12-diynoic acid (LI). In the presence of small amounts of alkalis, mycomycin undergoes isomerisation into the optically inactive isomycomycin (XCV), whose structure as trideca-*trans*--3,*trans*-5-diene-7,9,11-triynoic acid was confirmed by spectroscopic data and its complete synthesis by Bohlmann and Viehe[268] in 1954:



Bohlmann and Sugrow[154] synthesised *trans*-*trans*-mycomycin by reducing with aluminium amalgam the trideca--2,4,6-triene-8,10,12-triynoic esters (L) obtained by the reactions



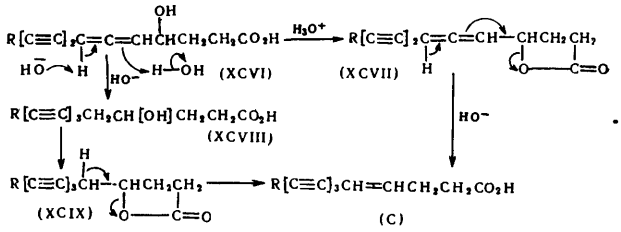
Synthetic *trans*-mycomycin is more stable towards alkalis, and its isomerisation half-life at pH 7.5 is 115 h, compared with the 3 h for natural *cis*-mycomycin[154].

Two other antibiotics having an allenic structure — *nemotin* (XCVII) and *nemotinic acid* (XCVI) — have been isolated from cultures of *Poria tenuis*, *P. corticola*, and the fungus B-841 (an unidentified Basidiomycete from white cedar)[269–271]. These two biologically active substances are very similar in their bactericidal spectrum, but differ considerably in fungicidal activity; they are very toxic, and cause contact dermatitis[269].

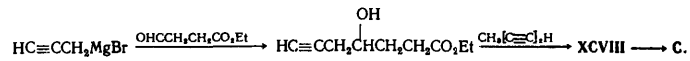
Both substances are extremely unstable, and can be prepared only in solution. When an attempt is made to isolate them from solution by lyophilic drying, they are converted into a dark polymeric mass[270]. Their ultraviolet and infrared spectra, catalytic hydrogenation, and chemical behaviour in alkaline and acid media[253,272] indicate that

nemotinic acid is a 4-hydroxyundeca-5,6-diene-8,10-diynoic acid (XCVI, R = H), while nemotin is its lactone.

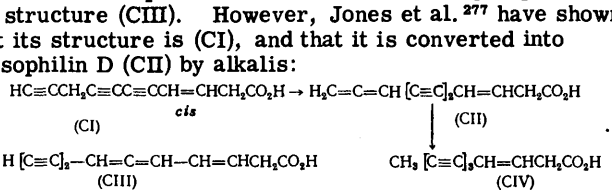
Study of the chemical transformations of these antibiotics showed[253] that at pH 10 nemotin undergoes rearrangement with cleavage of the lactone ring and formation of nemotin A (C, R = H). In contrast to this, nemotinic acid, which contains the same chromophoric group as does nemotin, is converted in alkaline medium into isonemotinic acid (XCVIII, R = H), from which the alkatriynoic lactone (XCIX) is readily formed; this compound can be further converted into nemotin A (C, R = H):



Odyssin (XCVII, R = CH_3) and *odyssic acid* (XCVI, R = = CH_3) are homologues of nemotin and nemotinic acid respectively, and are present with them in the culture liquid of the Basidiomycete B-841.[272,273] They are similar in chemical and physicochemical properties to the latter compounds, while their transformation products (R = CH_3) are more stable; the final structure of the compounds (XCVIII)–(C) has been proved by synthesis[177]:

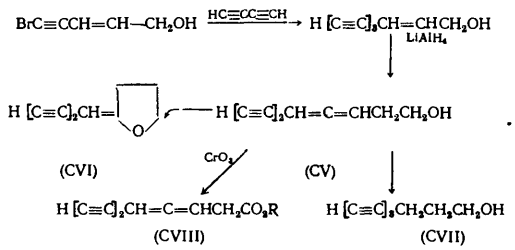


In addition to the above, two related polyunsaturated antibiotics — *drosophilins C* and *D* — have been isolated from the culture medium of the fungus *Drosophilia subatrata*[274,275] and *D. semivestita*[276]. It was formerly supposed that drosophilin C contained an allenic group and had the structure (CIII). However, Jones et al.[277] have shown that its structure is (CI), and that it is converted into drosophilin D (CII) by alkalis:



Thus drosophilin D (CII) contains a terminal allene group. It can be converted by further isomerisation into the alkenetriynoic acid (CIV).

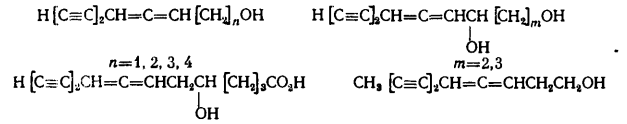
Marasin (CV) is the only allenic antibiotic at present known in both optically active forms. In 1959 (-)-marasin was isolated from a culture of *Marasmius ramealis*[278], and quite recently (+)-marasin has been obtained from the culture medium of *Aleurodiscus roseus*[226]. The formula (CV) was assigned to marasin on the basis of a study of the chemical transformations and the infrared and ultraviolet spectra; this has subsequently been confirmed by a complete synthesis of the racemate[153].



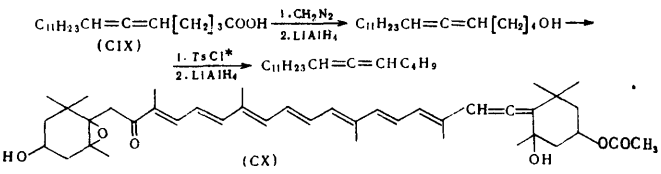
In alkaline media all three forms of marasin are readily converted into the corresponding cyclic enolic ether, isomarasin (CVI), which on hydrogenation absorbs five moles of hydrogen with the formation of n-butyltetrahydrofuran, identified by gas–liquid chromatography. It is interesting that the alkaline isomerisation of (+)-marasin yields also a small amount of the alkatriynol (CVII).

Two new allenic antibiotics — nona-3,4-diene-6,8--diynoic acid (CVIII) and its methyl ester — have been isolated, together with (+)-marasin, from the culture medium of *Aleurodiscus roseus*[226], and have been synthesised from natural marasin.

It has recently been noted that *Odontia bicolor*[279] manufactures mycomycin and certain other allenic antibiotics, to which can be assigned the structures



Among natural allenic compounds the simplest is labal-lenic (octadeca-5,6-dienoic) acid (CIX), which has been isolated from the oil of *Leonotis nepetaefolia*[280]. This acid is extremely stable to alkalis and, in conformity with its structure, can be readily converted into octadeca-5,6-diene.



* Ts = *p*-$CH_3C_6H_4SO_2$ (Ed. of Translation).

The first allenic carotenoid to be isolated was fucoxanthin (CX), from seaweed[281]. Its proposed structural formula (CX) is extremely reliable[282,283], and agrees well with experimental results hitherto obtained.

Further investigation will undoubtedly lead to the isolation of other natural allenic compounds, which will enable us to elucidate the routes of their biogenesis and their role in the vital activities of micro-organisms.

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ORGANOPHOSPHORUS COMPOUNDS CONTAINING ACETYLENIC AND DIENE SUBSTITUENTS

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I. INTRODUCTION

The interest taken by research workers in the chemistry of unsaturated organophosphorus compounds, which has increased extraordinarily during recent years, is explained by the potentialities of these compounds for use as monomers in the manufacture of plastics[1], intermediates in the synthesis of plasticisers[2], solvents for the extraction of compounds of the rare metals[3], finishing agents for textiles[4], additives to lubricating oils[5], and also as starting materials for the synthesis of various biologically active compounds[6-10]. Besides this, the great reactivity and the accessibility of unsaturated organophosphorus compounds of various classes makes them valuable materials for the study of the interaction of atoms in organic compounds of elements in the Third Period, in particular for elucidating the role of the vacant *d*-orbitals in the transmission of electronic influences in the molecule[11-14].

The first attempts to prepare acetylenic derivatives of phosphorus were made in 1921.[15] More recent work on the synthesis of tertiary acetylenic phosphines and of phosphonic esters containing 1,3-diene substituents attached to the phosphorus atom has been summarised in Gefter's monograph[1] (up to 1958) and in several reviews[16,17]. This section of the chemistry of organophosphorus compounds has developed so rapidly since 1958 that the number of compounds synthesised has more than doubled. During the past seven years original new routes have been worked out for the synthesis of highly unsaturated compounds containing acetylenic, allenic, and 1,3-diene substituents attached to the phosphorus atom. Data obtained from the study of unsaturated organic compounds of phosphorus by modern physical methods (ultraviolet, infrared, and nuclear magnetic resonance spectroscopy, dipole moments) have enabled certain conclusions to be drawn concerning the way in which phosphorus-containing groups are conjugated with multiple bonds. The present review summarises all these fresh results.

II. PREPARATION AND CHEMICAL PROPERTIES

1. Phosphines

Primary phosphines are usually obtained by the reduction of halogenophosphines and by the reaction of phosphine and its metal derivatives with alkyl halides and carbonyl compounds[18]. None of these methods has been used to obtain acetylenic or diene phosphines. Attempts to use the reduction of phenylethynylphosphonic ester with lithium tetrahydroaluminate to obtain a primary phosphine containing the phosphino-group directly linked to a triple bond were unsuccessful. Besides cleavage of the phosphorus–carbon bond, the triple bond was hydrogenated to a double bond with formation of α-styrylphosphine[19,20]:

$$C_6H_5C{\equiv}CPO(OC_2H_5)_2 \rightarrow C_6H_5CH{=}CHPH_2.$$

Two of the primary acetylenic phosphines which have been described were obtained by the reaction of sodium phosphide with acetylenic α-epoxides in liquid ammonia[21]:

$$RC{\equiv}C{-}\underset{CH_2}{\overset{}{C}}{-}\underset{O}{\overset{}{CH_2}} \xrightarrow[NH_3]{NaPH_2} RC{\equiv}CC(OH)(CH_3)CH_2PH_2$$

where R = CH_3 or C_4H_9.

No secondary phosphines have been described containing acetylenic or diene substituents. Tertiary phosphines,

however, represent the most thoroughly studied group of phosphines both with saturated and with unsaturated substituents.

The most widely applicable method of preparing tertiary phosphines is the reaction of organometallic compounds with three-coordinated phosphorus halides. Most of the tertiary acetylenic phosphines have been obtained by this method. A long series of papers in this field was initiated by de Mahler [15], who tried to obtain phosphorus carbide by the reaction of ethynylenedimagnesium di-iodide with phosphorus trichloride. Although the desired result was not achieved in this case [22-24], the synthesis became the most fruitful method of obtaining various tertiary acetylenic phosphines. Successful use was subsequently made of Iotsich complexes derived from acetylenic hydrocarbons, acetylenic alcohols [25,26] and sulphides [27], ethynylmagnesium [27,28] and butadiynylmagnesium bromides in tetrahydrofuran, and also ethynylenedimagnesium dibromide [24,27,29]. From the appropriate organomagnesium compounds and diaryl- or dialkyl-phosphinous chlorides compounds could be obtained containing alkenynyl [30,31], butadiynyl, and hexatriynyl [30] substituents attached to the phosphorus atom, as well as acetylenic diphosphines [24,27,29]:

$$R\,[C{\equiv}C]_nMgX + R_2PCl \rightarrow R\,[C{\equiv}C]_nPR_2.$$

The application of this reaction to phenylphosphonous dichloride and to phosphorus trichloride enabled tertiary phosphines to be obtained containing two [25] and three [32] acetylenic substituents. The yields in reactions of this type are usually high. A diminished yield is often due to instability of the final products.

Sodium acetylides in liquid ammonia can be used instead of organomagnesium compounds. The chlorophosphines are then replaced as starting materials by the corresponding alkoxy- or alkylthio-derivatives [27]:

$$HC{\equiv}CNa + ROPR'_2 \rightarrow HC{\equiv}CPR'_2 + RONa.$$

It must be supposed that sodium alkyl or aryl acetylides may be used equally successfully in this interesting reaction.

Another original route has also been proposed for the preparation of tertiary phosphines containing a terminal acetylenic group. Cleavage of 4-diphenylphosphino-2-methylbut-3-yn-2-ol in the presence of alkali leads to the formation of ethynyldiphenylphosphine in 68% yield:

$$(C_6H_5)_2PC{\equiv}CC(CH_3)_2OH \xrightarrow{KOH} (C_6H_5)_2PC{\equiv}CH + (CH_3)_2CO.$$

Unfortunately, no experimental details are given [25]. Finally, bisdibutylphosphinoacetylene is cleaved by phenyl-lithium with the formation of dibutylphosphine and ethynyldibutylphosphine [27]:

$$(C_4H_9)_2PC{\equiv}CP(C_4H_9)_2 + C_6H_5Li \rightarrow (C_4H_9)_2PC{\equiv}CLi + C_6H_5P(C_4H_9)_2$$
$$\downarrow H_2O$$
$$(C_4H_9)_2PC{\equiv}CH$$

The above phosphines containing a terminal acetylenic group readily undergo substitution of the acetylenic hydrogen. This method has been used to synthesise tertiary alkylacetylenic phosphines and acetylenic carbinols containing a dialkylphosphino-group attached to the triple bond [25,27].

Tertiary acetylenic phosphines can also be obtained from the lithium dialkyl phosphide and chloroacetylenes [33]:

$$R_2PLi + ClC{\equiv}CC_6H_5 \rightarrow R_2PC{\equiv}CC_6H_5 + LiCl.$$

This reaction is less convenient for obtaining acetylenic phosphines than, say, the organomagnesium synthesis. However, it is of theoretical interest, since it indicates the quite high reactivity of a halogen adjacent to a triple bond. A reaction of similar type has proved extremely fruitful in the synthesis of esters of phosphonic acids containing acetylenic substituents.

Petrov and Kormer proposed a method for preparing tertiary phosphines having an allenic group in the hydrocarbon substituent, which was based on the addition of lithium phosphides to alka-1-en-3-ynes [34]:

$$RC{\equiv}CCH{=}CH_2 \xrightarrow{LiPR'_2} RLiC{=}C{=}CHCH_2PR'_2 \xrightarrow{H_2O} RCH{=}C{=}CHCH_2PR'_2,$$

where R = CH_3, C_2H_5 and R' = C_2H_5, C_4H_9. Pent-1-en-3-yne yields as side-product an acetylenic phosphine: i.e. allene–acetylene rearrangement is observed [35].

Among phosphines containing conjugated diene substituents, only cyclic phospholes are known. These are obtained by the reaction of tetraphenylbuta-1,3-dienylenedilithium with dihalogenophosphines, or alternatively by the interaction of the 1,4-di-iodobutadiene derivative with disodium phenyl phosphide [36-39]:

$$\left.\begin{array}{l} LiC(C_6H_5){=}C(C_6H_5)C(C_6H_5){=}C(C_6H_5)Li + C_6H_5PCl_2 \\ IC(C_6H_5){=}C(C_6H_5)C(C_6H_5){=}C(C_6H_5)I + C_6H_5PNa_2 \end{array}\right\} \rightarrow \begin{array}{l} C_6H_5{-}C{-}C{-}C_6H_5 \\ C_6H_5{-}C\;\;\;C{-}C_6H_5. \\ \quad\quad\;\; P{-}C_6H_5 \end{array}$$

Heterocycles containing two conjugated double bonds and containing several heteroatoms besides phosphorus have been synthesised by this method.

It can thus be seen that methods for the synthesis of tertiary phosphines containing acetylenic or diene substituents are more varied than those for obtaining phosphines containing ethylenic substituents [40-45].

Acetylenic and diene phosphines are liquids or crystalline solids having the characteristic properties of phosphines. Those containing alkyl groups possess an unpleasant odour. The constants of the acetylenic and diene phosphines which have been described are given in Table 1. The only omissions from this are the phosphines mentioned in Ref. 30 without indication of their constants or yields (1-diethylphosphinopropyne, 1-diethylphosphino-2-phenylacetylene, and 1-diphenylphosphino-propyne, -butadiyne, -penta-1,3-diyne, and -hepta-1,3,5-triyne).

Little work has been done on the chemical properties of acetylenic phosphines. The strength of the phosphorus–carbon bond is strongly dependent on the structure of the phosphine. Thus bisdiphenylphosphinoacetylene is not cleaved by dilute alkali, silver nitrate, or cuprammonium solution; cleavage takes place only on alkaline fusion or prolonged boiling with a saturated alcoholic solution of potassium hydroxide [24]. Dibutylphosphinoacetylene disproportionates in the presence of alkaline catalysts in liquid ammonia, with the formation of bisdibutylphosphinoacetylene, which, as already noted, may be cleaved by butyl-lithium [27]. Heating 4-diphenylphosphino-2-methylbut-3-yn-2-ol with alkali leads to the elimination of acetone, as already mentioned, but does not affect the P–C≡ bond [25]. The enhanced stability of the phosphorus–acetylenic bond in comparison with acetylenic derivatives of other elements is explained by the small difference in electronegativities between carbon and phosphorus according to Pauling (2.8 and 2.1 respectively) [24], which can hardly be accepted as correct.

TABLE 1. Organophosphorus compounds containing acetylenic and diene radicals*.

Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
primary phosphines						
$CH_3C{\equiv}CC(OH)CH_2PH_2$	73	50—51 (1)	—	0.9880	1.5063	21
$n\text{-}C_4H_9C{\equiv}CC(OH)(CH_3)CH_2PH_2$	73	60—64 (0.5)	—	0.9360	1.5063	21
tertiary phosphines having a terminal acetylenic group						
$(C_6H_5)_2PC{\equiv}CH$	49	66—67 (77)	—	—	1.4808	27
$(n\text{-}C_3H_7)_2PC{\equiv}CH$	60	55 (11)	—	—	1.4770	27
$(n\text{-}C_4H_9)_2PC{\equiv}CH$	70	37 (0.3)	—	—	1.4765	27,29
$(n\text{-}C_5H_{11})_2PC{\equiv}CH$	72.5	65 (0.35)	—	—	1.4759	27
$(C_6H_5)_2PC{\equiv}CH$	68	—	35	—	—	25,32,40—43
tertiary phosphines having a disubstituted acetylenic group						
$(n\text{-}C_4H_9)_2PC{\equiv}CCH_3$	81	66—67 (1)	—	—	1.4867	27
$(n\text{-}C_4H_9)_2PC{\equiv}CC_2H_5$	84	58 (0.25)	—	—	1.4848	27
$(n\text{-}C_4H_9)_2PC{\equiv}CCH{=}CH_2$		92 (3)	—	0.8602	1.5110	31
$(n\text{-}C_4H_9)_2PC{\equiv}CSC_2H_5$	81	78 (10^{-3})	—	—	1.5265	27
$(n\text{-}C_4H_9)_2PC{\equiv}C-C_6H_5$	70	—	44	—	—	33
$(C_6H_5)_2PC{\equiv}CC_6H_5$	79	—	43	—	—	25, 26, 33
	50		44			
$(C_6H_{11})_2PC{\equiv}CC_6H_5$	35	—	74	—	—	33
tertiary phosphine derivatives of acetylenic carbinols						
$(n\text{-}C_4H_9)_2PC{\equiv}CC(OH)(CH_3)_2$	58	91 (0.03)	—	—	1.4871	27
$(n\text{-}C_4H_9)_2PC{\equiv}CC(OH)(CH_3)_2$	70	105 (10^{-3})	25	—	1.5090	27
$(C_6H_5)_2PC{\equiv}CC(OH)(C_6H_5)_2$	95	—	143	—	—	25
$C_6H_5)_2PC{\equiv}CCH(OH)R$ (where R = fluoren-9-yl)	85	—	133	—	—	25
$(C_6H_5)_2PC{\equiv}CXOH$ **	90	—	202	—	—	25
tertiary phosphines containing two or three acetylenic groups						
$(RCH_2C{\equiv}C)_2P-C_6H_5$ (where R = anthr-9-yl)	90	—	193	—	—	52
$(HC{\equiv}C)_3P$	—	52 (30)	36—37	—	—	28
$(C_6H_5C{\equiv}C)_3P$	90	—	91	—	—	28
$(p\text{-}CH_3C_6H_4C{\equiv}C)_3P$	—	—	125	—	—	32
$(p\text{-}ClC_6H_4C{\equiv}C)_3P$	—	—	192 (decomp.)	—	—	32
$(RCH_2C{\equiv}C)_3P$ (where R = anthr-9-yl)	89	—	256	—	—	28
acetylenic disphosphines						
$(n\text{-}C_4H_9)_2PC{\equiv}CP(C_6H_5\text{-}n)_2$	96	—	33	—	—	27, 29
$(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$	—	—	86	—	—	24
tertiary phosphines containing 1,2- and 1,3-diene groups						
$(C_6H_5)_2PCH_2CH{=}C{=}CHCH_3$	36.5	60—61 (5)	—	0.8697	1.5050	51
$(C_6H_5)_2PCH_2CH{=}C{=}CHC_6H_5$	34	78—79 (5)	—	0.8569	1.5025	51
$(n\text{-}C_4H_9)_2PCH_2CH{=}C{=}CHC_6H_5$	28	125—126 (5)	—	0.8534	1.4952	51
phosphine oxides, sulphides, selenides, and quaternary salts						
$(CH_3)_2P(O)CH{=}C{=}CH_2$	—		58—60	—	—	52
$(C_6H_5)_2P(O)CH{=}C{=}CH_2$	60		96—99	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)_2$	75		70—73	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)C_2H_5$	80		69—71	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}CHC_3H_7$	95		43—46	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)_2$	90	—	107—109	—	—	51
$(C_6H_5)_2P(O)C{=}C{=}C(CH_3)C_2H_5$ $HOC(CH_3)C_2H_5$	90	—	—	—	1.5711	51
$(p\text{-}Cl{-}C_6H_4)_2P(O){-}C{=}C{=}C(CH_3)C_2H_5$ $HOC(CH_3)C_2H_5$	99	—	—	—	—	51
$(C_6H_5)_2P(O)C{=}CP(O)(C_6H_5)_2$	87	—	164	—	—	23
$(p\text{-}CH_3C_6H_4C{=}C)_2P{=}O$	—	—	177	—	—	32
$(C_6H_5)_2P(S)C{=}C_6H_5$	quantitative	—	156	—	—	33
$(C_6H_{11})_2P(S)C{=}CC_6H_5$	quantitative	—	111.5	—	—	33
$(C_6H_5)_2P(S)C{=}CP(S)(C_6H_5)_2$	75	—	186	—	—	23
$(p\text{-}CH_3C_6H_4C{=}C)_3P{=}S$	—	—	180 (decomp.)	—	—	32
$(p\text{-}CH_3C_6H_4C{=}C)_3P{=}Se$	—	—	162 (decomp.)	—	—	32
$[(C_6H_5)_2P(CH_3)C{=}CP(C_6H_5)_2]{+}I^-$	90	—	156	—	—	23
$[(C_6H_5)_2P(C_2H_5)C{=}CP(C_6H_5)_2]{+}I^-$	84	—	128	—	—	34
$(C_6H_5C{=}C)_2PS$	50		138.4—138.8	—	—	47
$[2,4\text{-}(CH_3)_2C_6H_3C{=}C]_2PS$	70	—	144.4—145.0	—	—	53
$(CH_3C{=}C)_2PS$	35	—	198.4—198.8	—	—	47
$C_6H_5P(S)(C{=}CC_6H_5)_2$	85	—	129.6—130.0	—	—	47
$C_6H_5P(S)(C{=}CCH{=}CH_2)_2$	30	—	67,8—68.4	—	—	47
$C_6H_5CH{=}CHP(S)(C{=}CC_6H_5)_2$	61	—	183,0—183.4	—	—	48
$CH_3P(S)(C{=}CCH_3)_2$	28	—	38.2—38.8	—	—	48
$CH_3P(S)(C{=}CC_6H_5)_2$	60	—	91.3—91.6	—	—	48
$(CH_3)_2P(S)C{=}CCH_3$	62	—	77.5—78.2	—	—	48
$(CH_3)_2P(S)C{=}CC_6H_5$	86	—	92.4—93.2	—	—	48
$(CH_3)_2P(S)C{=}CCH{=}CH_2$	63	122 (5)	42.0—43.0	1.0349	1.5852	48
$CH_3P(O)(C{=}CCH_3)_2$	55	—	70.5—71.0	—	—	49
$CH_3P(O)(C{=}CC_6H_5)_2$	65	—	101.0—101.4	—	—	49
esters of phosphonous acids containing acetylenic radicals						
$HC{=}CP(OC_4H_9\text{-}n)_2$	74	58.8—60 (2)	—	0.9829	1.4520	40—43
$HC{=}CP(OH)(OC_4H_9\text{-}n)$	78	65—66 (1.5)	—	1.0322	1.4492	40—43

TABLE 1 (contd.)

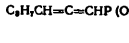
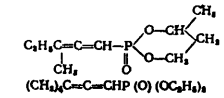
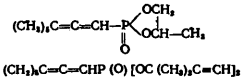
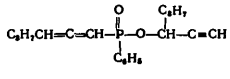
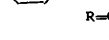
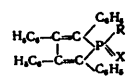
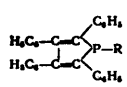
Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
phosphonic acids						
$C_6H_5C{\equiv}CP(O)(OH)_2$	—	—	142	—	—	54
$o\text{-}ClC_6H_4P(O)(OH)_2$	—	—	134	—	—	54
$C_6H_5C{\equiv}CP(O)(OH)C_6H_5$	quantitative	—	126—127	—	—	55
$(C_6H_5C{\equiv}C)_2P(O)OH$	79	—	145—146	—	—	55
esters of phosphonic acids containing acetylenic radicals						
$HC{\equiv}CP(O)(OC_2H_5)_2$	25	50—60 (0.1)	—	—	—	56,57
$HC{\equiv}CP(O)(OC_6H_7\text{-}iso)_2$	25—35	75—77 (0.1)	—	—	—	56,57
$ClC{\equiv}CP(O)(OC_2H_5)_2$	56	88.5—89.5 (2.5)	—	1.1439	1.4473	58
$CH_3C{\equiv}CP(O)(OC_2H_5)_2$	—	115—116 (4)	—	1.0734	1.4460	59—63
$CH_3C{\equiv}CP(O)(OC_3H_7\text{-}n)_2$	—	127—128 (4)	—	1.0279	1.4478	62
$CH_3C{\equiv}CP(O)(OC_4H_9\text{-}n)_2$	—	152—153 (6)	—	1.0029	1.4498	62
$CH_3C{\equiv}CCH_2P(O)(OC_2H_5)_2$	45—55	98 (3)	—	1.0489	1.4540	64
$C_2H_5C{\equiv}CP(O)(OC_2H_5)_2$	35	115—117 (3)	—	1.0325	1.4470	58
$CH_2{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	45—55	107—108 (2.5)	—	1.0630	1.4540	65
$CH_2CH{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	45—55	112—115 (2)		1.0610	1.4790	64
$CH_3{-}C(CH_3){\equiv}CP(O)(OC_2H_5)_2$	45—55	110—111 (3)		1.0549	1.4696	64
$C_6H_5C{\equiv}CP(O)(OC_2H_5)_2$	—	155 (1)		1.1500	1.5312	66
$C_6H_5C{\equiv}CP(O)(OC_6H_7\text{-}iso)_2$	—	159—161 (1)		1.0423	1.5090	66
$CH_2CH{=}CHC{\equiv}CCH_2{-}PO(OC_2H_5)_2$	53	107—107.5 (2)		1.0588	1.4752	61
$CH_3C{\equiv}CP(O)(OC_2H_5)_2$	28	134.5—136.5 (1.5)		1.0735	1.4930	67
$C_2H_5C{\equiv}CC{\equiv}CP(O)(OC_2H_5)_2$	54	130—131 (0.5)		1.0215	1.4897	67
derivatives of phosphonic acids containing allenic radicals						
$CH_2{=}C{=}CHP(O)(OC_2H_5)_2$	—	89 (0.4)		—	1.4544	52
$CH_2{=}C{=}CHP(O)(OC_6H_7\text{-}iso)_2$	—	126—127 (9)		1.0330	1.4580	62,63
$CH_2{=}C{=}CHP(O)(OCH_2C{\equiv}CH)_2$	—	117 (0.3)		—	1.4282 (25°)	52
$CH_2{=}C{=}CHP(O)[N(CH_3)_2]_2$	—	85 (0.17)		—	1.5046 (25°)	52
$CH_2C{=}C{=}CHP(O)(SCH_3)_2$	—	102 (0.3)		—	1.5840 (25°)	52
$CH_2{=}C{=}CHP(O)(C_2H_5)(OCH_2C{\equiv}CH)$	—	108 (0.3)		—	1.5071 (25°)	52,62,63
$CH_3CH{=}C{=}CHP(O)(OC_2H_5)_2$	—	105 (1.0)		—	1.4797 (25°)	52
$CH_2{=}C{=}C(CH_3)P(O)(OC_2H_5)_2$	—	73 (0.1)		—	1.4587 (25°)	52,63
$CH_2{=}C{=}C(C_6H_5)P(O)(OC_2H_5)_2$	—					63
$(CH_3)_2C{=}C{=}CHP(O)(OC_2H_5)_2$	—	95 (0.8)		—	1.4588 (25°)	52
$(CH_3)_2C{=}C{=}CHP(O)(C_2H_5)(OCH_2C{\equiv}CH)$	60	—	—	—	1.5344	51
$(CH_3)_2C{=}C{=}CHP(O)[OC(CH_3)_2C{\equiv}CH]_2$	78	—	—	—	1.4859	51
$(CH_3)_2C{=}C{=}CHP(O)(OC_6H_7\text{-}iso)_2$	91	—	—	—	1.4917	51
$C_2H_7CH{=}C{=}CHP(O)$ 	95	—	—	—	1.4910	51
	94.5	—	—	—	1.4950	5
$(CH_3)_2C{=}C{=}CHP(O)(OC_6H_5)_2$	—	123 (0.2)	—	—	1.4738 (25°)	52
	85	—	89—91	—	—	51
$(CH_3)_2C{=}C{=}CHP(O)[OC(CH_3)_2C{\equiv}CH]_2$	88	—	78—91	—	—	51
	95	—	—	—	1.5325	51
phosphonic chlorides containing acetylenic and diene radicals						
$CH_3C{\equiv}CP(O)Cl_2$	92.5	56—57 (1.5)	—	1.3953	1.4912	68
$CH_2{=}CHC{\equiv}CP(O)Cl_2$	28	61—65 (2,5)	—	1.3784	1.5150	68
$C_6H_5{-}C{\equiv}CP(O)Cl_2$	36	121—124 (0.5)	—	1.3650	1.5938	68
$CH_2{=}CHCH{=}CHP(O)Cl_2$	60	65—66 (1)	—	1.3107	1.5413	68
$CH_2{=}CHC(CH_3){=}CHP(O)Cl_2$	67	77.5—78 (2)	—	1.2887	1.5400	68
$CH_3CH{=}CHCH{=}CHP(O)Cl_2$	56	97—100 (3—3.5)	46—48	—	—	68
$CH_2{=}CHCH{=}CHP(S)Cl_2$	37	86—88 (1.5—2)	—	1.2992	1.5842	68
$ROCH{=}C(POCl_2)CCl{=}CH_2$						
$R{=}CH_3$	31	48—48.5 (0.002)	—	1.4562	1.5826	69
C_2H_5	43	59.5—60.5 (0.012)	—	1.3682	1.5730	69
C_3H_7	46	69—69.5 (0.012)	—	1.3152	1.5635	69
C_4H_9	55	82—82.5 (0.020)	—	1.3078	1.5620	69
$RSCH{=}C(POCl_2)CCl{=}CH_2$						
$R{=}CH_3$	80	67—67.5 (0.02)	—	1.4950	—	70
C_2H_5	58	77—77.5 (0.02)	—	1.4156	—	70
C_3H_7	62	83—84 (0.02)	—	1.3634	—	70
C_4H_9	76	81—82 (0.002)	—	1.3222	—	70
$CH_3C(CH_2Cl)CCl{=}CHPOCl_2$	59	121 (3)	—	1.5400	1.5405	71
	54	132 (2)	—	1.4103	1.5808	72
esters of phosphonic acids containing 1,3-diene radicals						
$CH_3C(CH_2Cl)CCl{=}CHP(O)(OR)_2$						71
$R{=}CH_3$	69	136 (3)	—	1.3155	1.4957	
C_2H_5	73	142.5 (2)	—	1.2365	1.4838	
C_3H_7	67	158 (2)	—	1.1749	1.4805	
						72
$R{=}C_2H_5$	90.5	132 (1)	—	1.1688	1.5142	
C_3H_7	56	131 (1)	—	1.1235	1.5083	

TABLE 1 (contd.)

Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
esters of phosphonic acids containing 1,3-diene radicals						
$ROCH{=}CHCCl{=}CHPO(OR')_2$						73—76
$R{=}CH_3$ $R'{=}CH_3$	58	90—91 (0.01)	—	1.2702	1.5180	
C_2H_5 CH_3	70	75—76 (0.004)	—	1.2372	1.5150	
C_3H_7 CH_3	60	84—85 (0.006)	—	1.1972	1.5108	
C_4H_9 CH_3	70	79.5—81 (0.002)	—	1.1742	1.5057	
C_3H_7 C_2H_5	55	87—88 (0.006)	—	1.1252	1.4990	
C_4H_9 C_2H_5	64	90—91 (0.006)	—	1.1122	1.4970	
$RSCH{=}CHCCl{=}CHPO(OR')_2$						73—76
$R{=}CH_3$ $R'{=}CH_3$	44	78 (0.007)	—	1.3011	1.5791	
C_2H_5 CH_3	45	80—81 (0.0085)	—	1.2531	1.5700	
C_3H_7 CH_3	60	84—85 (0.005)	—	1.2248	1.5623	
C_4H_9 CH_3	53	83—84 (0.0002)	—	1.1960	1.5490	
CH_3 C_2H_5	57	80 (0.005)	—	1.2121	1.5498	
C_2H_5 C_2H_5	60	84 (0.004)	—	1.1861	1.5460	
C_3H_7 C_2H_5	52	84—86 (0.004)	—	1.1535	1.5436	
C_4H_9 C_2H_5	57	94—95 (0.004)	—	1.1411	1.5420	
CH_3 C_3H_7	58	84—84.5 (0.003)	—	1.1524	1.5412	
C_2H_5 C_3H_7	46	90 (0.005)	—	1.1574	1.5402	
C_3H_7 C_3H_7	35	87 (0.0003)	—	1.1114	1.5334	
C_4H_9 C_3H_7	60	93 (0.0002)	—	1.0983	1.5294	
CH_3 C_4H_9	46	78—79 (0.002)	—	1.1103	1.5302	
C_2H_5 C_4H_9	56	82 (0.0015)	—	1.1014	1.5294	
C_3H_7 C_4H_9	63	72 (0.0001)	—	1.0869	1.5270	
C_4H_9 C_4H_9	57	92 (0.008)	—	1.0770	1.5236	
C_2H_5 $CH_2{=}CHCH_2$	37	62 (0.007)	—	1.1756	1.5620	
C_3H_7 $CH_2{=}CHCH_2$	45	97.0—97.5 (0.005)	—	1.1570	1.5570	
C_4H_9 $CH_2{=}CHCH_2$	50	104—105 (0.003)	—	1.1353	1.5508	
C_2H_5 $HC{\equiv}CCH_2$	39	125—126 (0.009)	—	1.2531	1.5804	
C_3H_7 $HC{\equiv}CCH_2$	38.4	125—126 (0.0007)	—	1.2278	1.5895	
C_4H_9 $HC{\equiv}CCH_2$	40	130—130.5 (0.009)	—	1.2073	1.5827	
$CH_2CH{=}CHCH{=}CHP(O)(OCH_3)_2$	54	101—103 (2)	—	1.0661	1.4932	68
$CH_2{=}CHCH{=}CHP(R)(OR_1)$						77
$R{=}CH_3$	25—30	80 (2)	—	1 1109	1.5300	
$R{=}C_3H_7$	25—30	93.0—93.5 (2)	—	1.0234	1.4971	
$R{=}C_4H_9$	25—30	115 (3)	—	0.9968	1.4984	
$CH_2{=}CHCH{=}CHP(Se)(OCH_3)_2$	—	98—100 (3)	—	1.3343	1 5164	77
sulphides and amides of phosphonic and phosphonothioic acids						
$ROCH{=}CHCCl{=}CHPO[N(C_2H_5)_2]_2$						73—76
$R{=}C_2H_5$	50	104—105 (0.006)	—	1.0652	1.5110	
C_4H_9	50	108—109 (0.008)	—	1.0532	1.5100	
$RSCH{=}CHCCl{=}CHPOR'_2$						73—76
$R{=}C_2H_5$ $R'{=}SC_2H_5$	60	122—123 (0.015)	—	1.2702	—	
C_3H_7 SC_2H_5	55	128—129 (0.015)	—	1.2087	—	
C_4H_9 SC_2H_5	57	158—160 (0.018)	—	1.1545	—	
C_4H_9 SC_3H_7	62	148 (0.012)	—	1.1332	—	
C_2H_5 $-N(CH_2)_4-CH_2$	75	133 (0.015)	—	1.2706	1.6023	
C_3H_7 $-N(CH_2)_4-CH_2$	82	148 (0.015)	—	1.2550	1.5996	
C_4H_9 $-N(CH_2)_4-CH_2$	78	155 (0.015)	—	1.2389	1.5945	
CH_3 $N(C_2H_5)_2$	63	101 (0.009)	—	1.1107	1.5606	
C_2H_5 $N(C_2H_5)_2$	36	107 (0.007)	—	1.0992	1.5564	
C_3H_7 $N(C_2H_5)_2$	43	112 (0.005)	—	1.0916	1.5516	
C_4H_9 $N(C_2H_5)_2$	36	118 (0.006)	—	1.0690	1.5482	
derivatives of 1-phosphacyclopenta-2,4-diene						
						
$X{=}O$ $R{=}CH_3$	10	240—245.5	—	—	—	39
S C_2H_5	88	197—198	—	—	—	39
Se C_4H_9	93	187—188.5	—	—	—	39
O $CH_2C_6H_5$	10	240.5—241.5	—	—	—	39
O C_2H_5—Fe(CO)$_3$	94	226—235 (decomp.)	—	—	—	39
O C_6H_5	70	292—293	—	—	—	38
						
$R{=}C_6H_5$	84	255—256	—	—	—	36
$C_2H_5Fe(CO)_4$	quantitative	186—188	—	—	—	39
$C_2H_5Fe(CO)_3$		210—215	—	—	—	39
$C_6H_5Fe_2(CO)_3$		178—183 (decomp.)	—	—	—	39
$CH_2C_6H_5$	38	203—213	—	—	—	39

* Table 1 does not include compounds cited in Geffer's monograph.[1]

** X = anthrafuchsone.

Primary acetylenic phosphines — derivatives of acetylenic alcohols — do not give derivatives with 2,4-dinitrobenzoyl chloride, toluene-*p*-sulphonyl chloride, phenyl isocyanate, or picric acid, nor are they hydrogenated over platinum black or Raney nickel[21]. Tertiary acetylenic phosphines, however, can react both at the phosphino--group and at the acetylenic group. They add oxygen, sulphur, selenium, and halogenated hydrocarbons at the phosphorus, and compounds having alkyl substituents attached to the phosphorus are more reactive than aromatic or alkatriynyl phosphines[24,30,32,33]. As stated previously, tertiary phosphines containing a terminal acetylenic group undergo reactions involving substitution of the acetylenic hydrogen. Thiols in the presence of peroxides add at the triple bond[27]:

$$(C_4H_9)_2PC{\equiv}CH + C_2H_5SH \rightarrow (C_4H_9)_2PCH{=}CHSC_2H_5.$$

The chemical properties of phospholes give no grounds for assuming that these compounds are appreciably aromatic in character. They undergo both reactions characteristic of conjugated dienes (Diels–Alder reaction, formation of complexes with iron carbonyls) and reactions involving the lone pair of electrons on the phosphorus (addition of oxygen, sulphur, and selenium and complex formation)[36-39].

It follows from the above survey of the chemical properties of acetylenic phosphines that study of the influence of the triple bond on the well-known chemical properties of phosphines has been far from adequate, while the literature contains no discussion at all of the problem of the steric structure of acetylenic phosphines. An X-ray examination of bisdiphenylphosphinoacetylene[46] has shown that this compound crystallises in monoclinic form with four formula units in the unit cell.

2. Phosphine Oxides, Sulphides, Selenides, and Quaternary Salts

These compounds are usually obtained by the addition of oxygen, sulphur, selenium, and halogenated hydrocarbons to phosphines.

Oxidation of bisdiethylphosphinoacetylene with hydrogen peroxide gives the dioxide of this compound, while reaction with elementary sulphur yields the disulphide. On interaction of this diphosphine with alkyl iodides, however, only mono-derivatives of the type $(C_6H_5)_2PC{:}CP(CH_3)(C_6H_5)_2I$ are formed[24].

The addition of oxygen, sulphur, and selenium to *para*--substituted trisphenylethynylphosphines[32] or to cyclic phospholes[36-39] also results in formation of the corresponding oxides, sulphides, and selenides.

Oxides and sulphides of phospholes have been obtained also directly from phosphonic and phosphonothioic chlorides respectively and the dilithium derivative of tetraphenylbutadiene. A similar path, without phosphines as intermediate products, has recently been used to obtain oxides and sulphides of tertiary acetylenic phosphines. When Iotsich complexes interact respectively with thiophosphoryl trichloride and the corresponding *P*-alkyl and *P*-aryl dichlorides and *PP*-dialkyl monochlorides, phosphine sulphides are obtained containing 1–3 acetylenic substituents and also conjugated alkenynyl radicals attached to the phosphorus atom[47-49]:

$$RC{\equiv}CMgX + R'_nP(S)X_{3-n} \rightarrow R'_nP(S)(C{\equiv}CR)_{3-n}.$$

It is interesting that tetrasubstituted diphosphine disulphides cannot be obtained when Iotsich complexes are used, in contrast to what occurs with alkylmagnesium halides. In this respect phenyl and styryl substituents occupy an intermediate position: when they are initial reactants, a phosphorus–phosphorus bond is formed only when one of them contains an alkyl substituent[49].

Reaction of phenylethynylmagnesium bromide with styrylphosphonothioic chloride yields a tertiary phosphine sulphide containing two triple bonds and one double bond in the α-position to the phosphorus atom[49].

1-Halogenoalkynes react with triphenylphosphine to form quaternary phosphonium salts containing an acetylenic substituent. Fluoroacetylene reacts considerably more rapidly than does chloroacetylene[50]:

$$(C_6H_5)_3P + HC{\equiv}CX \rightarrow [(C_6H_5)_3PC{\equiv}CH]^+X^-.$$

A novel case of the Arbuzov rearrangement of esters formed by acids containing three-coordinated phosphorus with alcohols of prop-2-ynyl type, accompanied by acetylene–allene isomerisation, was described in 1962. Use of dialkyl- and diaryl-chlorophosphines and various acetylenic carbinols yielded in this way phosphine oxides containing an allenic group attached to the phosphorus atom[51,52]. The mechanism of this reaction will be discussed below (in Subsection 3).

The physical constants of phosphine oxides, sulphides, and selenides and quaternary phosphonium salts containing acetylenic substituents adjacent to the phosphorus atom are given in Table 1.

The chemical properties of compounds of this type have been little studied. The strength of the P–C≡ bond is appreciably lower in phosphine oxides and sulphides than in the corresponding phosphines. Bisdiphenylphosphinoacetylene dioxide and disulphide are cleaved with the evolution of acetylene by boiling with alcoholic caustic potash and even when chromatographed on alkaline aluminium oxide[24]. The oxides, sulphides, and selenides of tri--*p*-tolylethynylphosphine and tri-*p*-chlorophenylethynylphosphine are cleaved at the P–C≡ bond by alkali, silver nitrate, and Ilosvay reagent[32].

3. Phosphonous and Phosphonic Acids and Their Derivatives

During recent years an intensive study has been made of phosphonous and especially phosphonic acids containing unsaturated substituents, as well as of their derivatives.

The starting materials for the synthesis of saturated phosphonous acids and their derivatives are usually phosphines or halogenophosphines, which are subjected to oxidation, hydrolysis, alcoholysis, etc. They are also obtained by the reaction of phosphorohalidites with organomagnesium or organolithium compounds.

A general method for preparing saturated phosphonic acids is the reaction of alkyl halides with trialkyl phosphites, sodium dialkyl phosphites, or phosphorus trichloride in the presence of aluminium chloride, and also the addition of simple phosphorus derivatives to unsaturated compounds at multiple bonds.

Unsaturated compounds of the above types can be synthesised by these methods and also by such procedures as the addition of phosphorus pentachloride at multiple bonds with subsequent elimination of hydrogen chloride, the rearrangement of prop-2-ynyl phosphites, etc.

Interaction of ethynylmagnesium bromide in tetrahydrofuran with halogenated phosphorus derivatives has been used for the synthesis of phosphonous and phosphonic esters containing a terminal acetylenic group attached to the phosphorus atom. Dibutyl phosphorochloridite gives dibutyl ethynylphosphonite, which is hydrolysed to the corresponding acid ester[40-43]. By the use of dialkyl phosphorochloridates and phosphorofluoridates a few ethynylphosphonic esters have been obtained in low yields and in not entirely pure form[56,57]:

$$(C_4H_9O)_2PCl + BrMgC{\equiv}CH \rightarrow (C_4H_9O)_2PC{\equiv}CH \xrightarrow{H_2O} C_4H_9OP(O)C{\equiv}CH \quad (H)$$

$$(RO)_2P(O)X + BrMgC{\equiv}CH \rightarrow (RO)_2P(O)C{\equiv}CH$$

Examples have been given of the application of organomagnesium compounds to the synthesis of unsaturated phosphonites and phosphonates. This route proved inconvenient for the preparation of phosphonous and phosphonic acids, owing to experimental difficulties in the isolation of the final products and to the poor mobility of halogen in phosphorohalidates.

Reaction of phosphorus pentachloride with 1,3-diene hydrocarbons yields addition products, which can be converted into chlorides of the corresponding phosphonic, phosphonothionic, and phosphonoselenonic acids[68,77-80]:

$$CH_2{=}CHCH{=}CH_2 + 2\,PCl_5 \rightarrow ClCH_2CH{=}CHCH_2PCl_4{\cdot}PCl_5 \xrightarrow{H_2X} ClCH_2CH{=}CHCH_2P(X)Cl_2 \xrightarrow[NR_3]{} CH_2{=}CHCH{=}CHP(X)Cl_2.$$

These acid chlorides can be obtained from alkenyne hydrocarbons and phosphorus pentachloride directly in one stage[69-76,81-85]. These hydrocarbons add the pentachloride at the triple bond[71,81,82]:

$$CH_2{=}CHC{\equiv}CR + 2\,PCl_5 \rightarrow CH_2{=}\underset{Cl}{CH}C{=}\underset{R}{C}PCl_4{\cdot}PCl_5 \xrightarrow{SO_2} CH_2{=}\underset{Cl}{CH}C{=}\underset{R}{C}POCl_2 + POCl_3.$$

In the case of hydrocarbons containing a monosubstituted acetylenic group, however, the products of this reaction either add further a molecule of hydrogen chloride (with butenyne) or replace by chlorine a hydrogen atom in the saturated radical[71,72,81-83].

Shostakovskii, Guseinov, and their coworkers have published a series of papers on the addition of phosphorus pentachloride to alkoxy- and alkylthio-alkenynes[69,70,73-76,84,85]. The latest paper of this series[70] gives a more precise structure for the products, and shows that the reaction is represented by the equation

$$ROCH{=}CHC{\equiv}CH \xrightarrow[2.\ SO_2]{1.\ PCl_5} ROCH{=}CHCCl{=}CHPOCl_2.$$

The chlorides of phosphonic acids obtained by addition of phosphorus pentachloride to alkenynes have been converted by the usual methods into the corresponding esters, thio-esters, and amides.

Chlorides of phosphonic acids containing 1,3-diene substituents have been obtained also by the oxidative phosphorylation of butenyne, but the yields are low[86]:

$$CH_2{=}CHC{\equiv}CH + 2PCl_3 + O_2 \rightarrow CH_2{=}CHCCl{=}CH{-}POCl_2 + POCl_3.$$

Acetylenic hydrocarbons and phosphorus pentachloride have been used to obtain phosphonic acids and esters containing arylacetylenic substituents attached to the phosphorus atom. The chlorostyrylphosphonic chlorides formed initially were converted into the free acids[54] or the esters[66], and then dehydrochlorinated. Arylethynylphosphonic acids[55] and also 4-phenylbutadienylphosphonic acid[87] have been prepared for the first time by this method:

$$RC{\equiv}CH + PCl_3 \rightarrow RCCl{=}CHPOCl_2 \rightarrow RCCl{=}CHP(O)(OR')_2 \rightarrow RC{\equiv}CP(O)(OR')_2.$$

However, this is not a general path for the preparation of acetylenic phosphonates. When β-chloro-p-methoxystyrylphosphonic acid is used, for example, dehydrochlorination cannot be effected: the phosphorus–carbon bond undergoes fission[54].

The most fruitful reaction for the preparation of acetylenic phosphonates is the Arbuzov rearrangement. Early attempts to apply this process to halides of the prop-2-ynyl type containing a monosubstituted acetylenic bond resulted in the formation merely of isomeric compounds containing an acetylenic group attached to the phosphorus atom (in the case of prop-2-ynyl bromide[59]) or an allenic group[93]. This occurred also when a sodium dialkyl phosphite was used instead of the tertiary phosphite[59]. With prop-2-ynyl bromides having a disubstituted acetylenic group the "normal" Arbuzov rearrangement products were formed[61,64].

Halogenoacetylenes containing the halogen atom adjacent to the triple bond can also undergo the Arbuzov rearrangement with trialkyl phosphites, with formation of the normal products[65]. The most reactive compounds are those in which the triple bond is linked with another multiple bond, a benzene ring, or an electron-acceptor substituent such as a chlorine atom[58,64,67]. With respect to their reactivity the halogenoacetylenes are arranged in the series R–F > > R–Cl > R–Br > R–I, which is due to the diminution in polarisation of the ≡C–X bond in this sequence. Rearrangement involving halogenated acetylenes most probably takes place by the usual mechanism with the formation of a quasi-phosphonium compound as intermediate:

$$RC{\equiv}CX + P(OR')_3 \rightarrow RC{\equiv}CP(OR')_3X \rightarrow RC{\equiv}CP(O)(OR')_2 + R'X.$$

Phosphonic esters containing phenylethynyl, butenynyl, and butadiynyl substituents attached to the phosphorus atom have been obtained by this method, and several of them have been converted into the corresponding acid chlorides by the action of phosphorus pentachloride[68]. Dichloroacetylene gives with a phosphite under the same conditions diethyl chloroethynylphosphonate and bisdiethoxyphosphinylacetylene[58]. Use of monofluoroacetylene yields an ethynylphosphonic ester containing a terminal acetylenic group[58].

Phosphonic esters containing alkylethynyl substituents could not be obtained by the Arbuzov rearrangement[58,67]. Roundabout methods have been suggested for the synthesis of compounds of this type. Prop-1-ynylphosphonic ester is formed in low yield in the interaction of prop-2-ynyl bromide with triethyl phosphite[59] or sodium diethyl phosphite[64]. A more convenient method for the preparation of prop-1-ynylphosphonates is the reaction of dichloroacetone with two moles of triethyl phosphite, followed by treatment with sodium ethoxide[59]:

$$ClCH_2{-}CO{-}CH_2Cl \xrightarrow{P(OC_2H_5)_3} CH_2{=}\underset{O{-}PO(OC_2H_5)_2}{C}{-}CH_2Cl \xrightarrow{P(OC_2H_5)_3} CH_2{=}\underset{O{-}P(O)(OC_2H_5)_2}{C}{-}CH_2{-}P(O)(OC_2H_5)_2 \xrightarrow{C_2H_5ONa} CH_3{-}C{\equiv}C{-}P(O)(OC_2H_5)_2$$

and also prototropic isomerisation of esters containing allenic substituents attached to the phosphorus atom[61], which can be conducted with or without isolation of the intermediate allenic compound[62,63,88]:

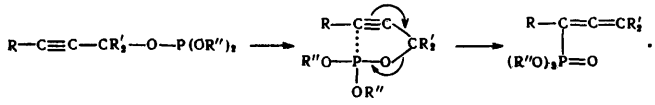
$$(RO)_2POCH_2{-}C{\equiv}CH \rightarrow CH_2{=}C{=}CHP(O)(OR)_2 \rightarrow CH_3C{\equiv}CP(O)(OR)_2.$$

The latter is not a general method, since, when homologues are used, the prototropic isomerisation either goes in a different direction or does not occur at all[61,63].

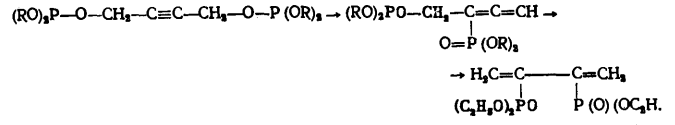
A process which is probably suitable for the preparation of various homologues of alkynylphosphonic acids has been employed for the synthesis of a but-1-ynylphosphonate[58]:

$$C_2H_5MgBr + ClC{\equiv}CP(O)(OC_2H_5)_2 \rightarrow C_2H_5C{\equiv}CP(O)(OC_2H_5)_2.$$

As stated above, esters formed by acids containing tervalent phosphorus with alcohols of the prop-2-ynyl type readily isomerise to give compounds containing an allenic group adjacent to the phosphorus[51,52,61-63]. Pudovik and his coworkers[88,89] have been able to show, by special investigations using mixtures of prop-2-ynyl phosphites, that this reaction involves intramolecular isomerisation with formation of an intermediate five-membered ring:



This reaction, which is in essence a variety of the Arbuzov rearrangement accompanied by acetylene–allene isomerisation, has made available various compounds containing an allenic group attached to phosphorus. Acetylenic glycols yield, together with allenic compounds, 1,3-diene-phosphonates containing two phosphinyl groups[51,90,91]:



In the case of prop-2-ynyl alcohol, as already stated, the reaction may not halt at the stage of the allenic compound. Available data on the synthesis of an allenic phosphonate by bromination and dehydrobromination of an allyl compound[92] require verification.

Physical constants of phosphonous and phosphonic acids containing acetylenic and diene substituents, and also of their functional derivatives involving the phosphorus, are given in Table 1.

Unsaturated phosphonous and phosphonic acids undergo reactions involving the phosphorus atom which are characteristic of their saturated analogues. Phosphonic esters containing acetylenic substituents react with phosphorus pentachloride to form chlorides of the corresponding acetylenic acids[68], which possess properties characteristic of the chlorides of saturated phosphonic acids. Their alcoholysis in the presence of triethylamine and their amidation at the phosphinyl group have been described[68,70,73-76,85].

Nucleophilic reagents add readily at multiple bonds in phosphonic esters of the present type, either one or two molecules being taken up with formation of a vinyl or a saturated derivative respectively[94,95].

Allenic phosphonates add at the double bond adjacent to the phosphorus atom[96]. Such nucleophilic reagents as dialkyl phosphites, thiols, secondary amines and alcohols add readily at multiple bonds in diene phosphinic esters in the presence of basic catalysts. Esters of acids containing 1,3-diene substituents add predominantly in the 1,4-positions[97].

Diels–Alder reactions have been reported in which butadiene-phosphonic and butadiene-phosphonothioic esters act as diene components[98]. References have been made in patents to the possibility of polymerising butadiene-phosphonic esters in the presence of benzoyl peroxide[78]. Finally, mention must be made of an interesting case of fission of the P–C≡ bond in an attempt to add alcohol to a prop-1-ynylphosphonic ester, a phosphoric ester being formed[95].

We conclude this review of methods of synthesis and chemical properties by noting that a few esters have been described formed by acetylenic alcohols with phosphoric and phosphonic acids[99-103]. Methods of synthesising these compounds do not differ fundamentally from those used for the saturated analogues. Work on the preparation of esters formed by prop-2-ynyl alcohols with acids containing tervalent phosphorus[104-106] require verification, since in fact the compounds obtained obviously have a different structure[51,52,62,107].

III. ELECTRONIC INTERACTIONS IN ORGANOPHOSPHORUS COMPOUNDS CONTAINING ACETYLENIC AND DIENE SUBSTITUENTS

The possibility of the conjugation of phosphorus with aromatic substituents and with a double bond has been discussed repeatedly in the literature. Most authors conclude that the four-coordinated phosphorus atom is only slightly involved in conjugation[11-13,108-110]. Little work has yet been done on the conjugation of phosphorus with a triple bond or on the effect of phosphorus on extended highly unsaturated systems.

A paper on the synthesis of phosphacyclopentadienyl compounds[39] has discussed the aromatic character of these structures. Pentaphenylphosphole[36-39] displays chemical properties characteristic of non-aromatic diene systems, which suggests that the phosphorus electrons are not involved in an aromatic sextet, in contrast to the position with pyrrole, which possesses appreciable aromatic character.

The situation is similar in open-chain highly unsaturated systems in which a phosphorus atom is attached to acetylenic or alkenyne substituents. Here, too, conjugation is far more evident in the substituent itself than between this substituent and the phosphorus atom. This is indicated in particular by the surprising constancy of the infrared frequencies of a triple bond attached to a phosphorus atom, these being practically independent either of the valency state of the phosphorus atom or of the nature of other substituents attached to this atom and being determined mainly by the structure of the acetylenic substituent. The C≡C and ≡C–H stretching frequencies in organophosphorus compounds containing a terminal acetylenic group lie within the ranges 2040–2090 and 3165–3300 cm^{-1} respectively[27,28,30,51,52,58-59,60]. It is interesting that these frequencies are appreciably higher (2120 and 3318 cm^{-1}) in the phosphine $(n\text{-}C_4H_9)_2PCH_2CH_2C{\equiv}CH$.[35] The C≡C stretching frequencies are determined in the case of a disubstituted triple bond by the structure of the acetylenic substituent: they are usually lower, within the range 2080–2180 cm^{-1}, for triple bonds conjugated with a benzene ring through a multiple bond or with a substituent containing lone pairs of electrons[27,28,30-35,47,48,53,58,61,64,65,67,68,111].

Unconjugated triple bonds linked to phosphorus, as also both conjugated and unconjugated triple bonds remote from the phosphorus, usually have frequencies lying in the range 2200 cm^{-1} and above[30,47,48,59-62,67] (but see Ref. 27). Phosphonates containing alkadiyne substituents exhibit two bands

due to the triple bonds, the frequency of the triple bond linked to the phosphorus atom being depressed[67].

The infrared spectra of derivatives of phosphonic acids containing 1,3-diene substituents attached to the phosphorus atom also contain two bands. The stretching frequencies of the double bonds lie in the usual range (1540–1640 cm^{-1}). The frequencies of allenic groups adjacent to the phosphorus atom lie within the usual limits (1925–1965 and 862–867 cm^{-1})[34,35,51,52,61]. The phosphoryl group in unsaturated compounds shows frequencies differing little from those in saturated compounds[112], which also indicates the insignificance of conjugation between this group and the multiple bonds.

Although the usual $\pi-\pi$ conjugation in highly unsaturated organic systems is greater in magnitude than conjugation of the phosphorus with the $\pi-\pi$ systems, the presence of the latter is suggested by the dipole moments (Table 2). This follows in particular from the considerable dipole moments of acetylenic and especially conjugated acetylenic phosphonates[65,113].

Published proton nuclear magnetic resonance data for organic phosphorus compounds containing one unsaturated substituent attached to the phosphorus atom do not permit us to assess the presence of conjugation with the phosphorus atom. It is true that the signal due to the acetylenic proton occurs at a lower field in ethynyldiphenylphosphine than in ethynyldialkylphosphines, and this has been taken to suggest the presence of conjugation[30], but it can equally be explained by the inductive effect of aromatic substituents, especially as the same paper mentioned a similar shift in the signal on passing from phosphines to phosphine oxides, under the influence of the strongly electronegative P=O group[30].

The chemical shifts and spin–spin coupling constants $J_{P,H}$ for protons separated from the phosphorus atom by more than one carbon–carbon bond (some of which may be unsaturated) vary in conformity with general views emerging from the study of other classes of compounds. Thus, for example, the accumulation of triple bonds in a substituent attached to the phosphorus atom displaces the terminal proton signal towards strong fields. This effect is explained by the diamagnetic anisotropy of triple bonds[30].

Oxidation and the addition of sulphur to acetylenic phosphines produce a sharp increase in the coupling constant $J_{P,H}$, owing to the increased electronegativity of the phosphorus atom[30].

With increase in the number of triple bonds the value of $J_{P,H}$ for the protons in the terminal methyl group decreases as a result of the increasing distance between the interacting nuclei. The decrease in $J_{P,H}$ is in general inversely proportional to the cube of the distance between the phosphorus nucleus and the proton, and a direct dipole–dipole mechanism has been suggested for this interaction[67].

In the case of phosphines an acetylenic proton is more strongly cleaved from the phosphorus through two triple bonds than through one triple bond (1.45 and 0.5 c/s respectively). This interesting fact has not yet been explained[30].

In the phosphorus nuclear magnetic resonance spectra[31] the chemical shift of the phosphorus nucleus in a diethoxyphosphinyl group adjacent to a triple bond has a constant magnitude of about +9 ppm (relative to 85% H_3PO_4). The small difference in the chemical shifts of acetylenic phosphonates having the triple bond in the $\alpha\beta$- and $\beta\gamma$-positions with respect to the phosphorus atom (29 ppm) has been interpreted as evidence of weak conjugation between the phosphinyl group and the triple bond[64].

TABLE 2. Dipole moments of diethyl esters of unsaturated phosphonic acids.

Compound	μ, D
$CH_2{=}CHCH_2PO(OC_2H_5)_2$	2.86
$CH_2CH{=}CHPO(OC_2H_5)_2$	2.92
$C_6H_5CH{=}CHPO(OC_2H_5)_2$	3.68
$CH_3C{\equiv}CPO(OC_2H_5)_2$	3.94
$CH_2{=}C(CH_3)C{\equiv}CPO(OC_2H_5)_2$	3.84
$CH_2{=}CHC{\equiv}CPO(OC_2H_5)_2$	3.88
$CH_3CH{=}CHC{\equiv}CPO(OC_2H_5)_2$	4.06
$C_6H_5C{\equiv}CPO(OC_2H_5)_2$	4.17
$C_6H_5C{\equiv}CC{\equiv}CPO(OC_2H_5)_2$	4.39

Thus to the extent that it is possible at all to assess the electronic interaction between phosphorus and unsaturated systems by the methods used to judge $\pi-\pi$ conjugation[11–13], it must be concluded that phosphorus is less well conjugated with a $\pi-\pi$-conjugated substituent than is the substituent itself conjugated. Nevertheless, conjugation of a triple bond with phosphorus-containing groups is rather better than is that of a double bond[111].

A second interesting group within the class of compounds under discussion comprises those containing three unsaturated substituents attached to the phosphorus atom, their structure being close to tetrahedral. Cruickshank has shown[114] that strong $\pi-d$ bonding can be assumed in tetrahedral ions of the type XO_4^{n-} (where X = P, S, Cl), owing to the effective overlapping of two of the five vacant d-orbitals of the central atom ($d_{x^2-y^2}$ and d_{z^2}) with eight non-bonding $2p\pi$-orbitals of the oxygen atoms (two orthogonal orbitals on each atom). Apart from the appropriate symmetry of these orbitals, interaction is ensured by the decrease in their energy and increase in the magnitude of the overlap integrals[115,116] due to the presence of the positive charge on the central atom.

A definite analogy can be traced between tetrahedral ions and tertiary phosphine sulphides having three acetylenic substituents attached to the phosphorus atom. In fact each of the triple bonds has two orthogonal π-orbitals, and the datively bound sulphur atom has two orthogonal p-orbitals. It is true that, in view of the presence of the datively bound sulphur, tertiary phosphine sulphides should have had dipole moments of the order of 10 D (transfer of one electron along the bond), whereas actually their moments do not reach half this value. But this fact is immediately explained by $p-d$ interaction between the sulphur and the phosphorus[117].

The present Reviewers have studied the dipole moments and the ultraviolet, infrared, and ^1H-nuclear magnetic resonance spectra of a series of sulphides of unsaturated tertiary phosphines[47–49]. The long-wavelength band in the ultraviolet spectra undergoes a bathochromic shift as unsaturated substituents accumulate at the phosphorus atom, the absorption intensity changing disproportionately to the number of unsaturated substituents (Table 3). This fact has been interpreted as confirming conjugation of the unsaturated substituents with the central phosphorus atom.

It has been mentioned above that the frequency of the triple bond in the infrared spectra of sulphides of tertiary acetylenic phosphines is practically independent of the

TABLE 3. Ultraviolet spectra of sulphides of unsaturated tertiary phosphines.

Compound	λ_{max}, nm	$10^{-3}\epsilon_{max}$
$(CH_3)_2P(S)C{\equiv}CCH_3$	221	4.34
$CH_3P(S)(C{\equiv}CCH_3)_2$	234	3.38
$P(S)(C{\equiv}CCH_3)_3$	250	4.46
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	246	20.50
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	253	38.45
$P(S)(C{\equiv}CC_6H_5)_3$	256	49.13
$(C_6H_5)_2P(S)CH{=}CHC_6H_5$	264	29.89
$C_6H_5P(S)(CH{=}CHC_6H_5)_2$	267	47.24
$P(S)(CH{=}CHC_6H_5)_3$	277	46.12

number of acetylenic substituents attached to the phosphorus atom. Study of the ^1H-nuclear magnetic resonance spectra of these compounds shows that this does not imply the absence of transmission of electron interactions through the phosphorus atom[48]. Table 4 gives the chemical shifts and spin–spin interaction constants for the protons in methyl groups combined with the phosphorus atom [40 Mc/s, 10 mole % in CCl_4 and $(CH_3)_4Si$, internal standard].

As acetylenic substituents accumulate at the phosphorus atom, and also with increase in their electron-acceptor properties, the spin–spin interaction constant with the phosphorus nucleus increases, while the chemical shift of the protons decreases. With the protons of methyl groups adjacent to the triple bond, however, the usual dependence of the chemical shift on the electron-acceptor properties of the substituents breaks down[53] (Table 4). Firstly it must be noted that the chemical shift of the protons of methyl groups in prop-1-ynyl substituents is of the same order of magnitude as the chemical shifts of protons in methyl groups directly attached to the phosphorus atom, although the signal due to the former should have been located in the region of smaller fields (in view of the greater electron--attracting power of the triple bond). Furthermore, as triple bonds accumulate at the phosphorus atom the shift due to protons of methyl groups adjacent to a triple bond should still have been displaced to smaller fields, whereas actually it is raised (Table 4).

The results obtained can be explained by the superposition of three effects: on the one hand, there is actually a diminution in electron density under the influence of electronegative substituents, while on the other hand the protons are magnetically screened by the diamagnetic anisotropy of the triple bond, which to some extent balances the electronegativity effect. Finally, perhaps, the accumulation of identical acetylenic substituents at the phosphorus atom is accompanied by a decrease in the paramagnetic contribution of the phosphorus to the anisotropy owing to the enhanced symmetry of the molecule, which results in an additional increase in screening. As a result, maximum sphericity of the electron cloud of the molecule is achieved on passing to a trialkynyl derivative as a consequence of the maximum utilisation of the *d*-orbitals, and the proton chemical shift increases sharply. The spin–spin coupling constant increases in the same sequence as in the previous case, while its magnitude is appreciably less owing to the increase in distance between the protons and the phosphorus nucleus, which corresponds to general views on the way in which it varies.

A similar conclusion concerning the possibility of conjugation with the phosphorus atom in tetrahedral molecules of the sulphides of unsaturated tertiary phosphines is reached from a study of the dipole moments of these compounds[49]. Comparison of the dipole moments of tertiary phosphines and phosphine sulphides containing phenyl- and *p*-tolyl-ethynyl groups indicates that the vector of the resultant moment is directed from the acetylenic substituents towards the phosphorus atom. With the moment in this direction, it would be expected to decrease with increase in the electron-attracting power of the substituents. This is in fact observed in the halides of three-coordinated phosphorus, tertiary acetylenic phosphines, and also thiophosphoryl halides. In the case of the sulphides of tertiary acetylenic phosphines, however, an appreciable increase is observed in the dipole moments with increase in the sum of the inductive constants [σ^*-values] of the substituents attached to the phosphorus atom [Table 5]. This increase can be explained by the presence of some positive electronic effect acting in the same direction as the vector representing the overall moment of the molecule. The effect may be caused by the presence of moments due to the substituents themselves, the contribution of which to the total moment of the molecule will increase with increase in the number of these substituents. On the other hand, it can be explained by π–d interaction between the acetylenic substituents or the halogens and the phosphorus atom, this increasing with increase in the number of these substituents from 1 to 3, when maximum effective utilisation of the *d*-orbitals becomes possible: i.e. it increases in parallel with the dipole moment. In the sulphides of acetylenic phosphines, accumulation of acetylenic substituents is accompanied by a more rapid increase in π–π interaction than in the negative inductive effect of the substituents, and a general increase in dipole moment is observed. In the thiophosphoryl halides, in contrast, the negative effect increases more rapidly (as halogen atoms accumulate), and a general decrease in dipole moments is observed[53].

Published data indicate that the conjugation of phosphorus with highly unsaturated π–π systems is less marked than conjugation within the π–π systems themselves.

TABLE 4. Chemical shifts and spin–spin interaction constants of protons forming methyl groups in sulphides of acetylenic phosphines.

Compound	σ_{CH_3}, ppm	$J_{CH_3,P}$, c/s	$\sigma_{C\,|\,CCH_3}$, ppm	$J_{C\,|\,CCH_3,P}$, c/s
$(CH_3)_2P(S)C{\equiv}CCH{=}CH_2$	−1.9	12.9	—	—
$(CH_3)_2P(S)C{\equiv}CCH_3$	−1.9	13.5	−2.2	2.4
$CH_3P(S)(C{\equiv}CCH_3)_2$	−2.0	14.4	−2.1	4.1
$P(S)(C{\equiv}CCH_3)_3$	—	—	−1.0	4.7
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	−2.0	15.0	—	—
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	−2.2	16.0	—	—

TABLE 5. Dipole moments of sulphides of acetylenic phosphines.[49]

Compound	$\Sigma\sigma^*$	μ, D
$(p\text{-}CH_3C_6H_4C{\equiv}C)_3PS$	+3.99	5.47
$(C_6H_5C{\equiv}C)_3PS$	+4.05	5.32
$(CH_3C{\equiv}C)_3PS$	+3.90	5.20
$C_6H_5P(S)(C{\equiv}CC_6H_5)_2$	+3.30	5.20
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	+2.70	5.14
$C_6H_5CH{=}CHP(S)(C{\equiv}CC_6H_5)_2$	+3.11	5.12
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	+1.35	4.91
$(CH_3)_2P(S)C{\equiv}CCH_3$	+1.30	4.90
$(CH_3)_2P(S)C_2H_5$	−0.10	4.66

Furthermore, the phosphorus may be involved in conjugation with unsaturated substituents arranged tetrahedrally about the phosphorus atom, and, although this conjugation is small, it can be detected by physical methods. However, the possibility of fundamentally different explanations of the behaviour of organophosphorus compounds must be borne in mind.

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THE WOLFF REARRANGEMENT

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I. INTRODUCTION

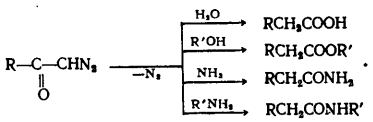
The great reactivity and comparatively ready accessibility of α-diazo-ketones have contributed to the rapid development of the chemistry of this peculiar class of organic compounds — see the most important reviews[1-11].

Many methods are now available for the preparation of α-diazo-ketones, the most important of these being the Arndt–Eistert method[12-38], consisting in the interaction of acid chlorides or anhydrides with excess of diazomethane, and the Curtius method, which is in effect the oxidation of monohydrazones of α-diketones with yellow mercury(II) oxide[39-47] or with some other oxidant[48-51]. Other derivatives of α-diketones — e.g. the toluene-*p*-sulphonylhydrazones[52-60] and the mono-oximes[61-63] — can also be used to obtain α-diazo-ketones. A new method had recently been worked out for the synthesis of α-diazocarbonyl compounds from alkane- or arene-sulphonylazides and carbonyl compounds[64-70].

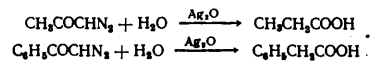
Among the various transformations undergone by α-diazo-ketones, the Wolff rearrangement is of most interest. The great amount of information which has accumulated in the more than 50 years since its discovery, the large quantity of experimental results obtained during recent years, and also the absence of reviews dealing specially with this question have led us to write the present paper. The literature is surveyed up to 1964 inclusive, and partly for 1965.

II. DEFINITION AND MECHANISM OF THE WOLFF REARRANGEMENT

The Wolff rearrangement — the conversion of α-diazo-ketones into acids and their derivatives — takes place on heating, in the presence of catalysts, or on ultraviolet irradiation in the presence of water, alcohols, ammonia, amines, etc:



In 1902 Wolff, while studying the properties of diazo-ketones[71,72], found that diazoacetone and diazoacetophenone, on interaction with water in the presence of silver oxide, did not undergo the usual replacement of the diazo-group by hydroxyl with formation of a hydroxy-ketone, but instead suffered rearrangement, with formation of propionic and phenylacetic acids respectively.



He showed in the same paper that, with aqueous ammonia to which a small quantity of silver oxide or silver nitrate had been added, diazo-ketones yielded amides even in the cold:



Independently of Wolff, in 1909 Schroeter.[73,74] observed an analogous rearrangement with "azibenzil" (benzoylphenyldiazomethane), and some authors therefore employ the term "the Wolff–Schroeter rearrangement".

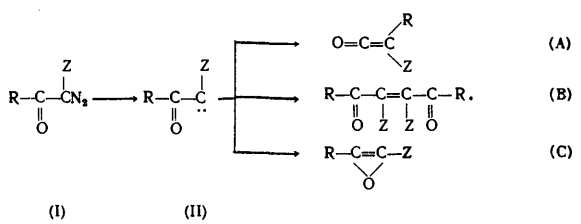
Catalytic rearrangement was employed mainly in the early work, the catalyst being most often silver oxide or a silver salt[72,75]. Finely divided platinum[72] and copper[76] are used considerably less frequently. With copper, however, the Wolff rearrangement takes place under severe conditions, the yield of acid being sharply diminished owing to the formation of other reaction products, mainly diacylethylenes[77-86]. An exception is provided by copper(I) iodide, with which rearrangement can occur under milder conditions[87].

The thermal rearrangement of α-diazo-ketones is employed less often than the catalytic method, for with the more severe conditions there is risk of decomposition of the starting materials. Nevertheless, this method of rearrangement gives very good results in the preparation of acid derivatives — anilides and certain esters[75,88,89].

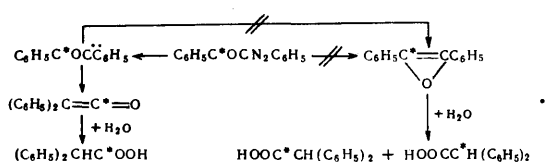
The considerable advantages of photolysis[90] as a method of effecting the Wolff rearrangement — the mild conditions for the reaction, the practical simplicity, and the possibility of considerably shortening the subsequent operations of separation and purification of the products — have rapidly brought it to the fore during recent years.

The mechanism of the Wolff rearrangement has now been studied quite fully. Wolff himself regarded the detachment of nitrogen as the cause of the reaction which he had discovered[71,72]: the residue remaining after detachment of nitrogen from the diazo-ketone molecule contains free valencies on the carbon atom, and undergoes rearrangement into a keten, which interacts with a hydroxy- or an amino-compound present in the reaction mixture to given an aicd or a derivative thereof.

The many subsequent investigations have convincingly shown that the first stage in the Wolff rearrangement is detachment of nitrogen from the diazo-ketone (I), accompanied by intermediate formation of a carbenone (II):

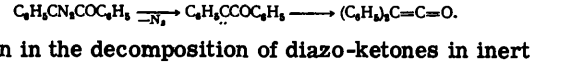


The defective octet in the intermediate compound (II) can be completed in three different ways — (A), (B), and (C) — the transition (II) → (A) resulting in formation of a keten, and from the latter the acid or its derivative, so that it represents the normal Wolff rearrangement. The bimolecular reaction (II) → (B) occurs comparatively rarely with diazo-ketones (for furthere details see Section V, 2). It usually takes place when R is a donor group, e.g. ethoxyl: thus, under the conditions of the Wolff rearrangement, diazoacetic ester is readily converted into diethyl fumarate[91]. Franzen has proved that formation of an oxiren (II) → (C) is not an intermediate stage in the Wolff rearrangement[92]. He effected the photochemical and thermal decomposition of azibenzil containing a labelled carbon atom in the carbonyl group, and showed that stabilisation of the carbenone occurs by migration of a phenyl group with formation of diphenylketen; the latter interacts with water to form diphenylacetic acid in which the whole of the activity is concentrated in the carboxy-group:

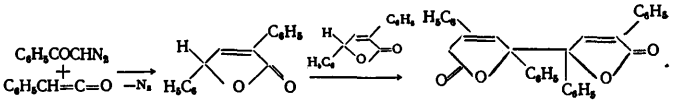


Thus the transformation (II) → (A), i.e. the Wolff rearrangement, is to be expected when R represents a hydrocarbon radical.

The intermediate formation of ketens in the rearrangement of diazo-ketones has in several cases been demonstrated experimentally [73,93-95]. Thus Schroeter isolated diphenylketen in the thermolysis of azibenzil in an aprotic solvent [73]:

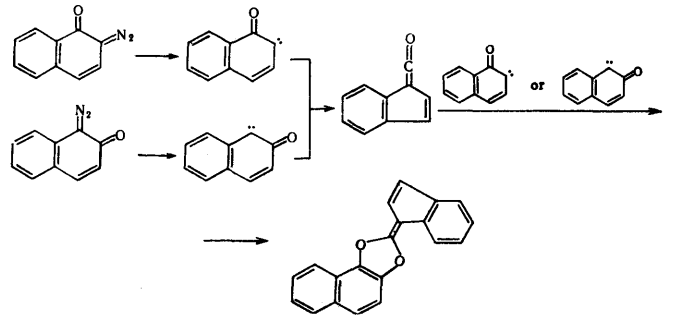


More often in the decomposition of diazo-ketones in inert solvents, however, ketens themselves are not obtained, but products of their further transformation, which is explained by the tendency to polymerise [96], and also to interact with the initial diazo-ketones or with the carbenones resulting from detachment of nitrogen from them. Thus the thermolysis of α-diazoacetophenone in dodecane led to the formation of a dilactone, to which has now been assigned the following structure [97]:



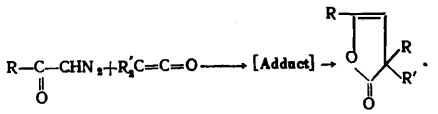
The formation of this compound is explained by interaction between the keten resulting from the rearrangement and the intermediate carbenone [98-100].

An analogous process obviously takes place in the thermal decomposition of diazonaphthaquinones [101]:

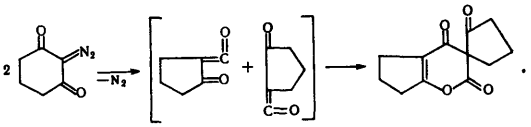


and in several other cases [102-105].

The interaction of ketens with diazo-ketones leading to the formation of βγ-unsaturated lactones is reported by Ried and Mengler [106-108], who assume that a short-lived addition product is produced, and stabilises itself by splitting off a molecule of nitrogen to give the unsaturated lactone:

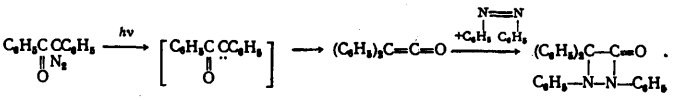


An interesting result has recently been obtained by Stetter and his coworkers [109] in the thermolysis of 2-diazocyclohexane-1,3-dione in xylene:

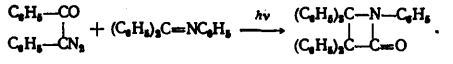


Formation of the final reaction product can be explained only by Wolff rearrangement of the initial diazo-ketone followed by dimerisation of the resulting keten.

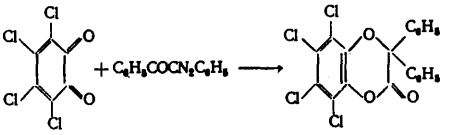
The formation of ketens during the Wolff rearrangement has been demonstrated in many cases by their reactions with specially added reagents. When azibenzil is illuminated in the presence of azobenzene, for example, a crystalline adduct is obtained which is a derivative of 3-oxodiazetidine [93]:



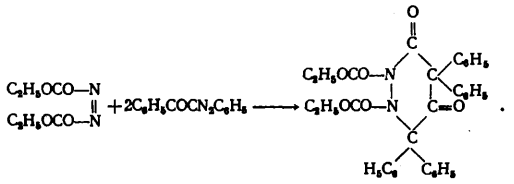
Cook and Jones [110] obtained the same compound from diphenylketen and *cis*-azobenzene. Ketens can add on also to azomethines (Schiff bases) to give β-lactams [111]:



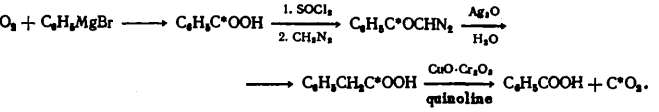
The keten arising in the photolysis of azibenzil could be recovered also by reaction with tetrachlorobenzo-*o*-quinone [93]:



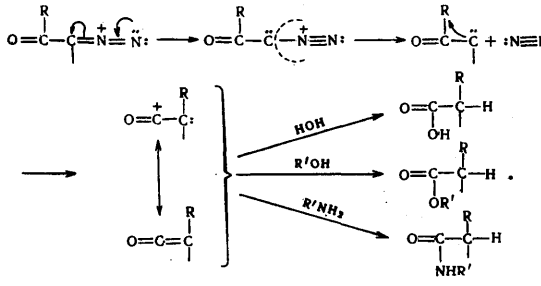
and by illuminating azibenzil together with azoformic ester [112]:



Conversion of the carbonyl group in a diazo-ketone into a carboxyl is established beyond doubt by the following cycle of reactions, in which radioactive carbon has been used [113]:

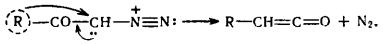


Thus the mechanism of the Wolff rearrangement can be represented by the scheme



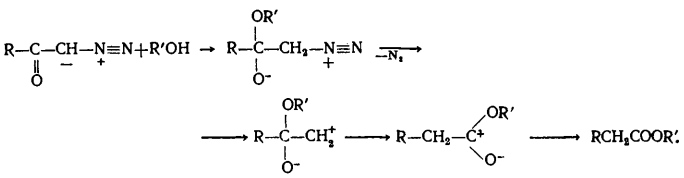
In the first stage, decomposition of the diazo-ketone with elimination of nitrogen results in the appearance of a carbenone characterised by an electron deficit. The carbenone is stabilised by the attack on a pair of electrons forming the β-bond. Depending on the reaction conditions, the resulting keten is converted into an acid, an ester, or an amide. Consequently the Wolff rearrangement represents a particular case of a large number of nucleophilic rearrangements occurring in saturated systems.

In the opinion of some authors[1], however, the carbenone structure is incompletely realised in the Wolff rearrangement, since transfer of the carbanion is assumed in several cases to occur synchronously with elimination of the nitrogen molecule:



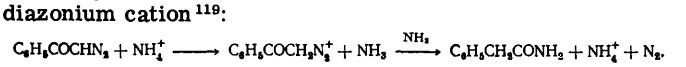
During the rearrangement of benzoylphenyldiazomethane in the presence of alcohol, an ether of benzoin is formed as a side-product[114] (i.e. the nitrogen molecule is eliminated before the rearrangement occurs). In some cases formation of oxidation products of the intermediate carbene is observed[115-117]. Both facts contradict the synchronous mechanism.

Müller formulated the following mechanisms for the rearrangement of diazo-ketones in the presence of an alcohol or water[118]:



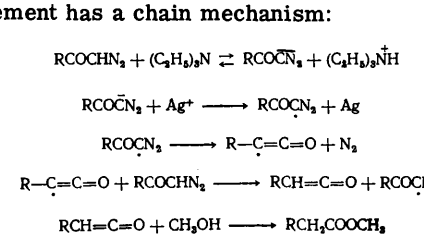
However, evidence is lacking for the intermediate formation of a betaine.

Other mechanisms have been suggested for the Wolff rearrangement. Thus Baddeley et al. consider that the rearrangement involves the intermediate formation of a diazonium cation[119]:



Such a mechanism is open to question, since the rearrangement of diazo-ketones is usually accomplished in neutral or even in weakly alkaline medium, where the appearance of a diazonium cation is improbable. Nevertheless, in isolated cases, when rearrangement occurs in acid medium[120,121], the possibility that a diazonium cation may be formed cannot be completely denied.

Newman and Beal[122], who were successful in effecting the Wolff rearrangement in homogeneous medium (in methanol in the presence of silver benzoate and triethylamine)[123-125], consider that under these conditions the rearrangement has a chain mechanism:

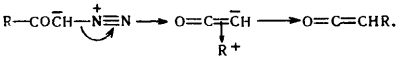


In their opinion this is supported by the following results: (1) reaction does not occur with diazo-ketones of the type $RCOCN_2CH_3$, which indicates that hydrogen must be present on the α-carbon atom; (2) reaction ceases on the addition of quinol, this obviously being due to reduction of the silver ion or of one of the intermediate products (reaction starts afresh on addition of excess of a silver salt); and (3) the reaction does not go in the absence of triethylamine, which confirms the first stage in the above mechanism.

The possibility of a radical mechanism for the rearrangement of diazo-ketones is consistent with the fact that other examples of homolytic,1,2-rearrangements have recently been discovered[126-131]. It must be stressed, however, that this mechanism is possible only under the above conditions and only with diazo-ketones in which hydrogen is attached to the carbon atom adjacent to the diazo-group.

The generally accepted mechanism for the Wolff rearrangement, implying intermediate formation of a carbenone which rearranges into a keten, is evidently the most probable.

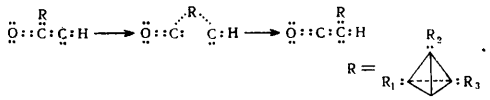
It is interesting that Dewar[132] suggested that the intermediate compound has the classical form of a π-complex:



This is consistent, in his view, with the fact that the Wolff rearrangement is an intramolecular rearrangement.

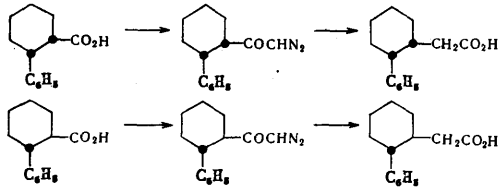
III. STEREOCHEMISTRY OF THE WOLFF REARRANGEMENT

A fundamental part of the mechanism of the rearrangement is the migration of the group R to an adjacent carbon atom. It might be supposed that during this process the group R would exist for a very short time as a kinetically independent particle. In order to assess the hypothesis critically, certain optically active compounds, in which R contained an asymmetric carbon atom, were subjected to the rearrangement. There could be three possibilities in such reactions: (1) racemisation might occur during the rearrangement, so that an optically inactive product would be obtained: (2) the compound might maintain its activity and configuration; or (3) while optical activity was preserved, there might be a change in configuration: i.e. Walden inversion might occur. Numerous investigations have established that, when optically active compounds undergo the Wolff rearrangement, the products are also optically active[133-139]. The retention of optical activity most probably means that the migrating group cannot exist in a free state even for a short period, but always remains within the force field of the molecule; while its bond with the adjacent carbon atom is still not completely ruptured, the group comes under the influence of another carbon atom, which prevents a change in configuration. This effect can be represented by the scheme[140]

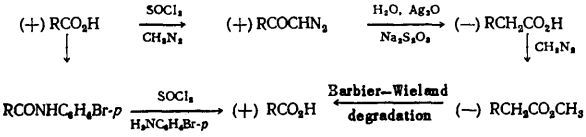


The above scheme gives a real idea of the migration of a pair of electrons from one carbon atom to another

(internal redox process). Such formulation of the process assumes the displacement to be strictly intramolecular (at no time does the system dissociate into either neutral or charged fragments). Under these conditions an optically active group should not be racemised in the course of the rearrangement. Moreover, inversion of configuration cannot occur with this formulation[141,142]. Thus Gutsche showed that configuration is maintained in the rearrangement of diazo-ketones obtained from *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids[143]:

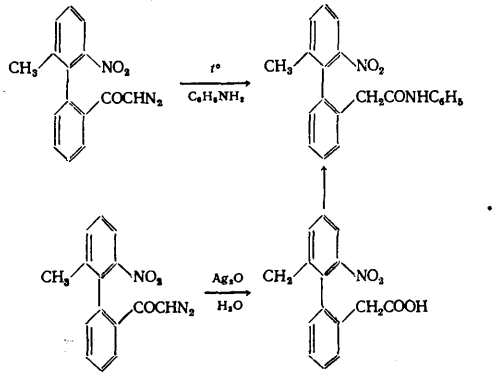


Lane[140] demonstrated the retention of configuration in the rearrangement of the diazo-ketone from (+)-2-methyl--2-phenylhexanoic acid, which was converted by the Arndt–Eistert method into optically active 3-methyl-3-phenylheptanoic acid. This was converted back, by Barbier–Wieland degradation, into the original acid. In this cyclic process initial and final products had the same optical rotation:



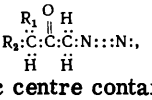
where R = n-$C_4H_9C(CH_3)(C_6H_5)$–.

The same worker showed[144] that, on thermolysis in boiling aniline, optically active diazomethyl 2′-methyl--6′-nitrobiphenyl-2-yl ketone gives without racemisation optically active 2′-methyl-6′-nitrobiphenyl-2-ylacetanilide. Rearrangement of the same diazo-ketone in aqueous–alkaline solution in the presence of silver oxide gave the optically active acid, which was then converted into the corresponding optically active anilide, found to be identical with the first anilide:

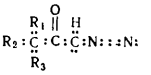


If the migrating group were able to detach itself even for an instant during the rearrangement, the blocking effect would have been removed, so that free rotation would have become possible, and racemisation would have occurred. Thus the possibility is eliminated of explaining the retention of optical activity by the presence of a free pair of electrons, which could act as a fourth substituent and prevent racemisation.

It is true that Bell[145] put forward the hypothesis that the radical may exist for a relatively short period in comparison with the time required for rotation of the two aromatic rings. It must be remarked that, if dextrorotatory 1-diazo-3-methyl-4-phenylbutan-2-one is subjected to the Wolff rearrangement, partial or complete racemisation (depending on the experimental conditions) takes place[146]. This phenomenon can be explained by the peculiar properties of the diazo-ketones



in which the asymmetric centre contains a mobile enolising hydrogen, since study of the behaviour of optically active diazo-ketones of the type



(where R_1, R_2, and R_3 are alkyl or aryl groups) under conditions of the Wolff rearrangement showed no trace of racemisation.

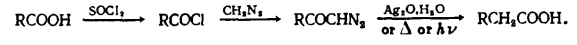
It must be emphasised that, when a secondary asymmetric atom is present, racemisation is observed usually in cases in which the Wolff rearrangement is conducted at temperatures exceeding 180° or in the presence of a catalyst, this obviously being due to tautomerisation of the diazo-ketone before rearrangement. The photolysis of diazo-ketones enables the Wolff rearrangement to be accomplished in the absence of a metal catalyst, and thus racemisation to be avoided during the reaction. Thus Wiberg and Hutton[147] established that, on ultraviolet irradiation, 1-diazo-3-methyl-4-phenylbutan-2-one gives mainly a rearrangement product in which the configuration is maintained.

IV. CHIEF SYNTHETIC APPLICATIONS OF THE WOLFF REARRANGEMENT

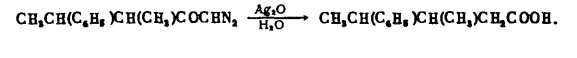
The Wolff rearrangement is of quite general synthetic value, being widely applicable for the preparation of acids and their derivatives in the aliphatic, aliphatic–aromatic, aromatic, alicyclic, and heterocyclic fields. It is successfully employed also for ring contraction.

1. Wolff Rearrangement as a Method of Synthesising Homologous Acids

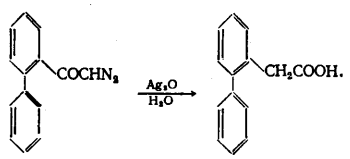
The Wolff rearrangement constitutes one stage in the Arndt–Eistert synthesis of homologous acids[19,75,148–152]:



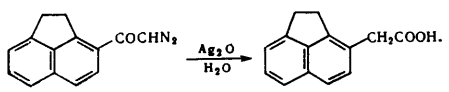
Thus, for example, an 81% yield of β-methyl-γ-phenylvaleric acid has been obtained by decomposing the corresponding diazo-ketone in the presence of silver oxide[153]:



Biphenyl-2-ylacetic acid has been obtained in 68% yield under the same conditions from biphenyl-2-yl diazomethyl ketone[154]:



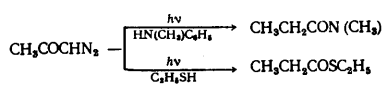
Acenaphthen-3-ylacetic acid is formed in approximately the same yield[155]:



The decomposition of diazo-ketones need not be conducted in aqueous medium: it is possible, and often even advisable, to effect the reaction in alcohol or aniline, since the rearrangement of diazo-ketones into acid derivatives usually occurs with rather better yields[65,156-161]. Ammonia and amines, especially aniline, add most smoothly, while the reaction goes less well with water and alcohols. Thus a 7% yield of *o*-nitrophenylacetanilide is obtained from diazomethyl *o*-nitrophenyl ketone, whereas ethyl *o*-nitrophenylacetate is obtained in 60% yield[162]. 1-Naphthylacetamide had been isolated in 84% yield from the corresponding diazo-ketone, whereas the yield of 1-naphthylacetic acid varies from 50% [162] to 70%.[27]

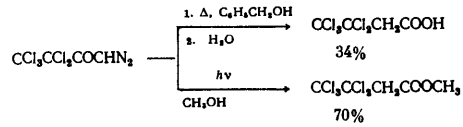
It is possible by using the classical method to effect the rearrangement of diazo-ketones under quite mild conditions, but the reaction products are then strongly contaminated by traces of colloidal silver or of silver salts. Moreover, the yields of the rearranged products are not always satisfactory[163,164], and in several cases, therefore, the thermal method of rearrangement is preferable. Thus an 85% yield of 2-1′-naphthylpropionanilide is obtained by thermolysis, whereas the yield of the acid itself on catalytic rearrangement of the same initial diazo-ketone is only 26%.[89] It is not at all possible under classical conditions to rearrange diazo-ketones obtained from *p*-anisoyl and *p*-toluoyl chlorides, whereas their thermolysis in benzyl alcohol permits the homologous acids to be isolated in yields of 76% and 79% respectively[89].

The photolytic method of effecting the rearrangement is the most widely applicable and the most convenient[93,94,115,165-172]. Whereas the yield of diphenylketen obtained by the thermal decomposition of azibenzil[73] is 77%, photolysis of the latter compound for 3 h enables a 92% yield of the keten to be isolated[93]. Irradiation of azibenzil in aqueous dioxan gives diphenylacetic acid[92,93,169] in excellent yield. If the illumination is conducted in ethanol, the ethyl ester is obtained. Weygand effected the photolysis of diazoacetone in the presence of *N*-methylaniline and ethanethiol respectively[173], and obtained a 77% yield of *N*-methylpropionanilide and a 67% yield of ethyl thiolopropionate:

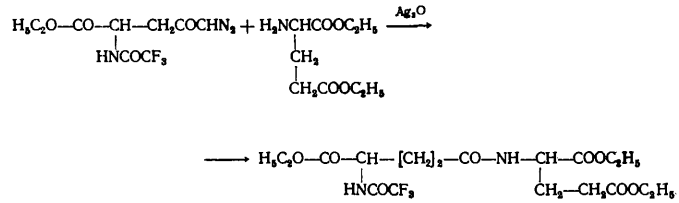


The photolytic method enables the Wolff rearrangement to be accomplished under the mildest conditions, and hence usually unaccompanied by any side-processes or resinification, which cannot be completely avoided in the catalytic or thermal decomposition of diazo-ketones.

It is especially important that the photolysis of diazo-ketones can often be successfully applied where the thermal and catalytic methods of rearrangement do not give positive results[4,174-180]. Thus 3,4,4-trichloro-1-diazobut-3-en-2-one $CCl_2{:}CClCOCHN_2$, because of its sensitivity to alkalis, does not rearrange under classical conditions, but can be converted into the corresponding acid by ultraviolet irradiation[175]. The great stability of 3,3,4,4,4-pentachloro-1-diazobutan-2-one makes rearrangement of this diazo-ketone impossible under classical conditions, but this can be achieved by thermolysis in benzyl alcohol in the presence of collidine at 150–190° [89] or by ultraviolet irradiation:



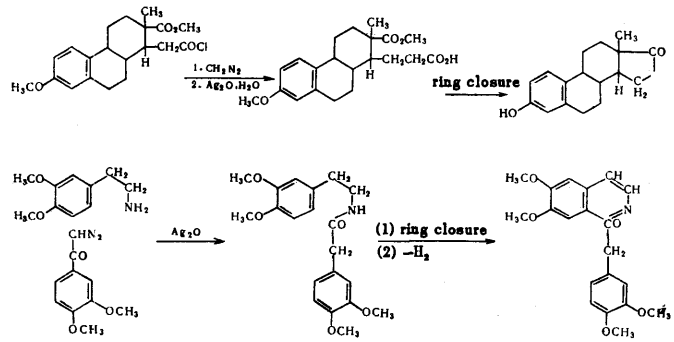
Mild reaction conditions (in photolysis or catalytic decomposition) make it possible to employ the Wolff rearrangement for the synthesis of complicated compounds containing functional groups, such as amino-acids and their derivatives[137-139,157,181], peptides, and polypeptides[5,135,136]. For example, the ethyl ester of δ-diazo-γ-oxo-*N*-trifluoroacetyl-L-norvaline in the presence of diethyl glutamate gives a good yield of triethyl *N*-trifluoroacetyl-γ-L-glutamyl-L-glutamate[134,182]:



An interesting example of the Wolff rearrangement is reported by Balenović[181], who succeeded in preparing α-methyl-β-alanine in 91% yield:

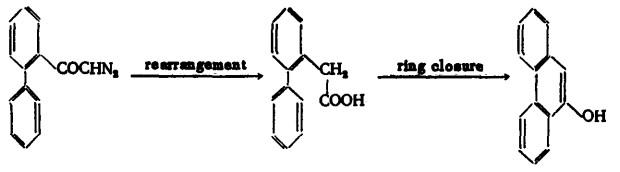
$$NH_2CH_2COCN_2CH_3 \rightarrow NH_2CH_2CH(CH_3)CONHC_6H_5 \rightarrow NH_2CH_2CH(CH_3)COOH.$$

In the work of this author the Wolff rearrangement is widely used for the conversion of α-amino-acids into β-amino-acids[5,157]. The rearrangement has been employed to obtain several intermediate products for the synthesis of natural substances, in isolated cases the natural substances themselves, e.g. oestrone, papaverine[183]:

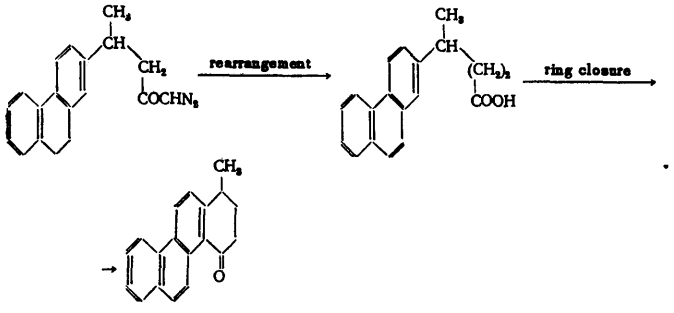


and several other related compounds[141,184]. It enables difficultly accesssible compounds to be prepared as well as compounds which cannot be obtained in other ways. Thus

the Wolff rearrangement constitutes one stage in the synthesis of 9-hydroxyphenanthrene[154]:



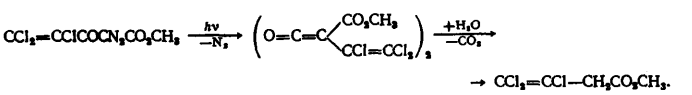
as also in the preparation of trimethoxyphenylacetic acid[185] and of 1,2,3,4-tetrahydro-1-methyl-4-oxochrysene[186]:



The Wolff rearrangement goes successfully also with diazo-ketones containing multiple bonds[122-125], the best results being obtained in a homogeneous medium, in the presence of silver benzoate and triethylamine. Wotiz[125], by using this method, isolated methyl non-7-ynoate in 80% yield, whereas under classical conditions the yield of this ester is 65%.[75]

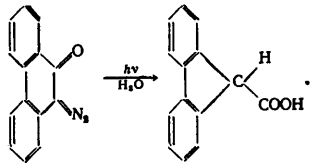
Comparatively few α-diazo-ketones cannot undergo the Wolff rearrangement. They include perfluorinated diazo--ketones: at least two methylene groups must be present between a perfluorinated radical and the carbonyl group for the rearrangement to give a satisfactory yield[157,179,187,188]. Diazo-ketones obtained from completely fluorinated propionic, butyric, and valeric acids, for example, do not undergo the Wolff rearrangement, and the diazo-ketone $C_3F_7CH_2COCHN_2$ gives only a small quantity of the homologous acid, whereas the diazo-ketone $C_3F_7[CH_2]_2COCHN_2$ rearranges normally and in good yield. Nevertheless, the diazo-ketones obtained from trifluoroacetic and trichloroacetic acids has been shown[159] to undergo the Wolff rearrangement, although only the esters of the homologous acids are obtained from them in satisfactory yield, whereas production of the acids themselves, their amides, and their anilides is poor.

Ethyl trifluoro- and trichloro-acetylcarbenecarboxylates, which appear when trifluoro- and trichloro-α-diazoacetoacetic esters are illuminated, likewise do not undergo the Wolff rearrangement, probably owing to the strong electronegative effect of the trifluoromethyl and trichloromethyl groups[177]. However, recent work has shown[176] that the photolysis of the 4,5,5-trichloro-2-diazo-3-oxopent-4-enoic ester results in partial formation of the normal rearrangement products:

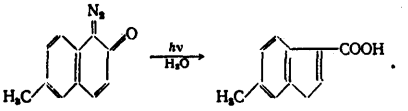


2. Wolff Rearrangement as a Method of Ring Contraction

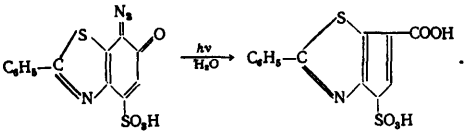
The Wolff rearrangement is of great value in the cyclic α-diazo-ketones series, when it involves ring contraction. The photochemical rearrangement of "quinone diazides" or "diazo-oxides" is a method of synthesising acids in the cyclopentadiene series[189-193]. Thus when phenanthrene--9,10-diazoquinone is illuminated in aqueous dioxan containing added acetic acid, fluorene-9-carboxylic acid is obtained in 80–88% yield[189]:



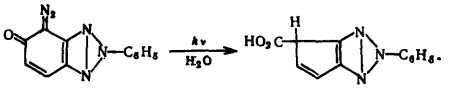
A 47% yield of 5-methylindene-1-carboxylic acid has been obtained by the photolysis of 6-methylnaphtha-1,2-diazoquinone[190]:



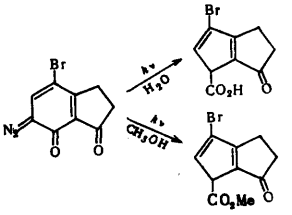
When 7-diazo-6,7-dihydro-6-oxo-2-phenylbenzothiazole-4-sulphonic acid is illuminated, the corresponding carboxylic acid is formed[190]:



4-Diazo-4,5-dihydro-5-oxo-2-phenylbenzotriazole gives 2-phenylcyclopentadienotriazole-4-carboxylic acid[191] in 43% yield:

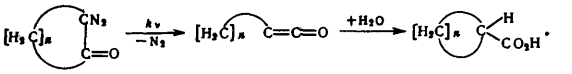


Horner and his coworkers have used the rearrangement of diazoquinones also to prepare pentalene derivatives[121]. They find that illumination of 4-bromo-6-diazo-6,7-dihydroindane-1,7-dione in dilute hydrochloric acid results in formation of the corresponding acid in 15% yield:



whereas exposure of the same compound in methanol to which concentrated hydrochloric acid has been added gives a 75% yield of the methyl ester of the acid.

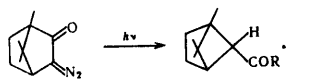
Alicyclic diazo-ketones on photolysis are converted into carboxylic acids with contraction of the ring[55,115,169]:



The tendency of diazo-ketones to undergo rearrangement is so great that rings are often formed which are

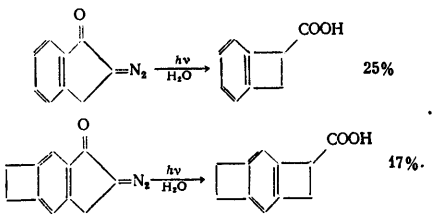
more strained than the original rings: five-membered from six-membered rings, and four-membered from five--membered rings[54,58,190,192-202]. Three cases have been reported in the pinane series in which the Wolff rearrangement did not take place[27]. Since, however, no indication was given of the reaction conditions, nothing can be said as to the reason for the absence of rearrangement in these cases.

The photolysis of diazocamphor[169] in aqueous medium gives a 76% yield of 1,6,6-trimethylbicyclo[2,1,1]hexane--5-carboxylic acid (R = OH):

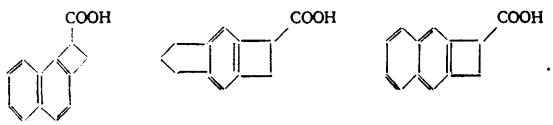


Irradiation of diazocamphor dissolved in ethanol, aniline, diethylamine, or dioxan containing hydrazine hydrate results in the formation of the ethyl ester, anilide, diethylamide, or hydrazide of this acid [R = OC_2H_5, NHC_6H_5, $N(C_2H_5)_2$, or $NHNH_2$ respectively].

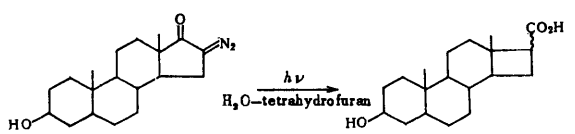
Horner and his coworkers applied the Wolff rearrangement to the preparation of cyclobutenobenzene derivatives, which for a long time had been regarded as unstable[115,194]:



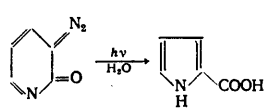
In spite of the low yields in individual cases, this reaction found wide application for the synthesis of complicated fused systems[55,194]:



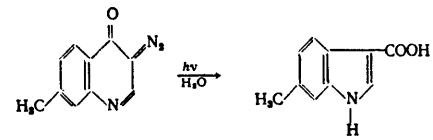
There are several interesting examples of ring contraction also among steroids[203-208] and triterpenes[63]. Thus illumination of 16-diazo-3β-hydroxyandrostan-17-one yields 3β-hydroxy-D-norandrostane-16-carboxylic acid[208]:



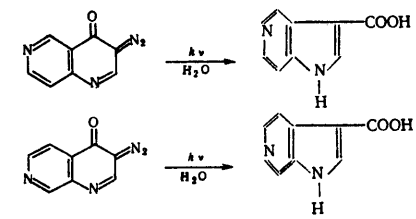
The Wolff rearrangement has been applied to heterocyclic α-diazo-ketones considerably less feequently. It was only in 1953 that Süs and his coworkers effected the Wolff rearrangement in certain nitrogen heterocycles of this type. Thus by the photolysis of 3-diazo-2,3-dihydro--2-oxopyridine they obtained pyrrole-2-carboxylic acid[190]:



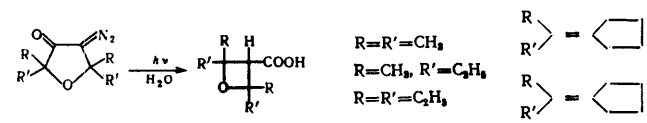
Using the same method Süs was able to synthesise several indolecarboxylic and azolopyridinecarboxylic acids[209,210]. Thus he isolated 6-methylindole-3-carboxylic acid in 80% yield[209]:



The photolysis of 3-diazo-3,4-dihydro-4-oxo-1,6(and 7)--diazanaphthalenes gives the corresponding 1,5(and 6)-diazaindene-3-carboxylic acids in ~ 50% yields[210]:



We have accomplished the conversion of tetrahydrofuran derivatives into oxetancarboxylic acids[117,211,212].



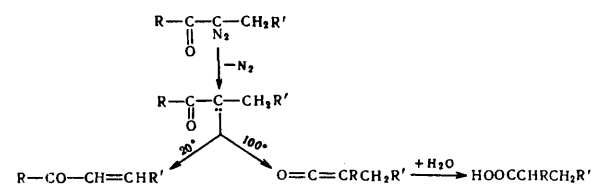
The reaction was conducted under classical conditions (in the presence of silver oxide), thermally, and photolytically. The best results were obtained by the photolysis of 2,2,5,5-tetra-alkyl-4-diazotetrahydro-3-oxofurans, the yields of the resulting 2,2,4,4-tetra-alkyloxetan-3-carboxylic acids being very high (60–97%), the reaction being simple to carry out, and no side-products being formed. This is the first example of the Wolff rearrangement among oxygen-containing heterocyclic α-diazo-ketones.

V. REACTIONS COMPETING WITH THE WOLFF REARRANGEMENT

Intramolecular rearrangement is not the only way in which the carbenone — the compound formed initially on detachment of nitrogen from a diazo-ketone — can be stabilised. The present Section discusses the chief transformations of α-diazo-ketones which compete with the Wolff rearrangement.

1. Hydrogen and Alkyl Migration

With diazo-ketones of the type $RCOCN_2CH_2R'$ rearrangement is accompanied by the migration of hydrogen, which results in the formation of an αβ-unsaturated ketone:



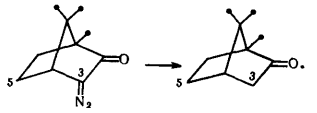
The relative proportions of the products depend on the reaction conditions. At room temperature the carbenone

is converted mainly into the $\alpha\beta$-unsaturated ketone. Thus on decomposing 3-diazo-4-phenylbutan-2-one in the presence of silver oxide, Franzen isolated 55% of 4-phenylbut--3-en-2-one[213]:

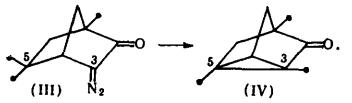
$$C_6H_5CH_2CN_2COCH_3 \longrightarrow C_6H_5CH{=}CHCOCH_3 + C_6H_5CH_2CH(CH_3){-}COOH.$$

At temperatures exceeding 100° the predominant reaction is rearrangement with formation of α-methyl-β-phenylpropionic acid. Franzen showed also that the reaction goes similarly under ultraviolet irradiation in the absence of a catalyst[213].

A new reaction of the same type — alkyl migration — has recently been discovered[77]. In contrast to photolysis, which gives the normal product of the Wolff rearrangement, heating diazocamphor in the presence of copper results in migration of a hydrogen atom† with formation of camphor[42]:



Compounds were therefore studied in which the $C_{(5)}$ position was occupied. Thus the diazo-ketone (III) was prepared from isofenchone, and its decomposition in the presence of copper bronze gave the ketone (IV) in 53% yield. In this case migration of a methyl group takes place, with formation of a $C_{(3)}-C_{(5)}$ bond:



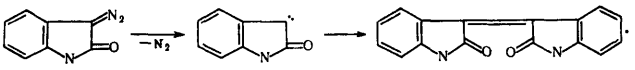
Hence in this instance *C*-alkylation competes successfully with the Wolff rearrangement.

2. Dimerisation and Trimerisation

As already mentioned, copper, like silver, accelerates the elimination of nitrogen from diazo-ketones, and is therefore sometimes used as a catalyst in the Wolff rearrangement. However, in the presence of copper catalysts rearrangement of the diazo-ketone is usually suppressed by dimerisation of the intermediate carbenone to a diacylethylene[78-86]. It has been established that predominantly unrearranged products are formed in the presence of copper[76], cuprous oxide[87], cupric oxide[82,215-218], copper chloride[87,219], and copper acetate or benzoate[87]. The copper catalysts are assumed[220] to stabilise the carbenone, whose rate of rearrangement into a keten is so strongly diminished that intermolecular interaction begins to predominate over intramolecular conversion. Thus when diazoacetophenone is heated in an inert solvent in the presence of cupric oxide, 1,4-diphenylbut-2-ene-1,4-dione is formed, to which Paal[221] has assigned the *trans*-configuration:

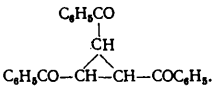
$$2C_6H_5COCHN_2 \xrightarrow{CuO} C_6H_5COCH{=}HCCOC_6H_5.$$

1,6-Diphenylhex-3-ene-2,5-dione $C_6H_5CH_2COCH{:}CHCOCH_2C_6H_5$, 1,2-distearoylethylene [octatriacont-19--ene-18,21-dione] $C_{17}H_{35}COCH{:}CHCOC_{17}H_{35}$, etc. have similarly been prepared from the corresponding diazo-ketones[78]. In some cases the dimerisation of carbenones occurs so readily in the presence of copper catalysts that this reaction is used as a method of synthesising symmetrical and even unsymmetrical unsaturated γ-diketones[79-85,241]. Isoindigo, for example, has been synthesised in this way[223]:



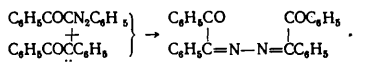
The course of the reaction is similar with 2-diazoindan--1-one[222].

In isolated cases[73,78] a more complicated intermolecular interaction of the intermediate carbenones — trimerisation — has been observed. Thus after boiling diazoacetophenone in isopentyl ether, Grundmann was able to isolate a very small quantity of *cis*-1,2,3-tribenzoylcyclopropane[78]

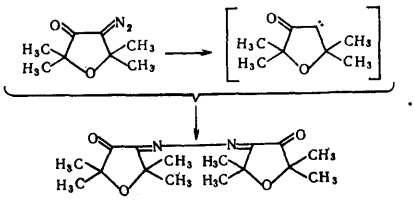


3. Formation of Ketazines

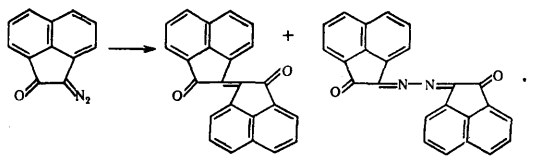
In the thermal decomposition of diazo-ketones — with or without a catalyst present — a further type of intermolecular reaction is possible, the intermediate carbenone interacting with the original diazo-compound[224-227]. Thus the decomposition of azibenzil in the presence of cupric oxide results in the formation of benzil monoazine[78]:



We have observed a similar course of reaction in the catalytic thermal decomposition of 4-diazotetrahydro--2,2,5,5-tetramethyl-3-oxofuran[212]:



The thermolysis of 2-diazoacenaphthen-1-one[228] results in a mixture of two products — biacenaphthenylidenedione and acenaphthenequinone monoazine:



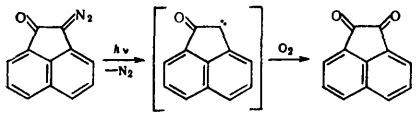
The pyrolysis of 3-diazo-1-methyl-2-oxoindoline has also led to isolation of the corresponding ethylenic derivative and the azine — 1,1′-dimethylisoindigo and 1,1′-dimethylisatin azine[229].

4. Oxidation of Intermediate Carbenones

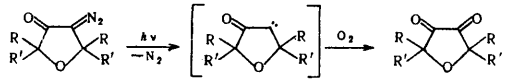
Cases of the oxidation of carbenes have been described in the literature. Diphenyldiazomethane when exposed to light, for example, adds on oxygen and is converted into

† There are other examples in which photolysis and thermolysis of diazo-ketones result in different reaction products[214] (see also Subsection 5, below).

benzophenone[224]. An analogous process, which completely suppresses the Wolff rearrangement, obviously occurs with diazoacenaphthenone[115], where only the corresponding α-diketone can be isolated after illumination:



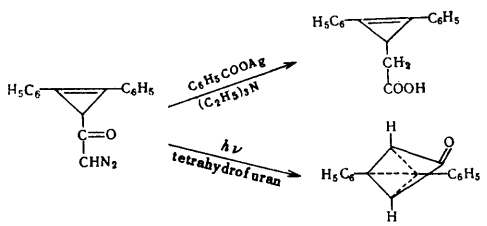
We have also observed the formation of small quantities of 2,2,5,5-tetra-alkyltetrahydrofuran-3,4-diones in the rearrangement of 2,2,5,5-tetra-alkyl-4-diazotetrahydrofuran--3-ones[212]:



where R = R′ = CH_3 and R = CH_3, R′ = C_2H_5.

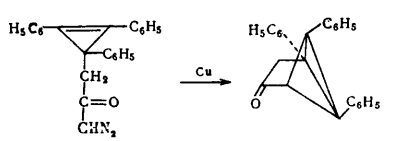
5. Intramolecular Addition of Carbenones at a Double Bond

An unusual result has been recorded in recent papers by Masamune[230,231], who has studied the rearrangement of diazomethyl 2,3-diphenylcyclopropyl ketone. He found that heating this compound with silver benzoate in triethylamine goes normally with a good yield of the methyl ester of the homologous acid. However, photolysis of the same diazo-ketone in tetrahydrofuran results in formation of a ketone belonging to the tricyclo[1,1,1,$0^{4,5}$]pentane system:



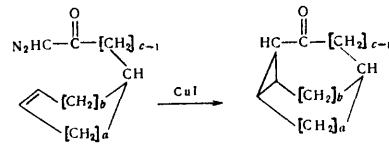
Hence in this case the α-ketocarbene formed on ultraviolet irradiation of the diazo-ketone exhibits a greater tendency to intramolecular addition at the double bond[3,4,232-235] than to rearrangement.

A similar type of reaction has been observed also by Small[236] and by several other workers[237-240]. Thus boiling 1-diazo-3-triphenylcycloprop-2′-enylpropan-2-one in benzene in the presence of copper powder results in a 57% yield of 4,5,6-triphenyltricyclo[2,1,1,$0^{5,6}$]hexan-2-one:



In the above examples the intramolecular addition of the carbenone at the double bond is obviously governed by the structural peculiarities of the initial diazo-ketones — by the presence of a nucleophilic double bond in the diazo--ketone molecule, and also of a strained unsaturated three--membered ring, which disappears as a result of the reaction.

The catalytic decomposition of monocyclic diazo-ketones containing a double bond in the ring has been used by Doering for the synthesis of tricyclic systems[239]:



(where a = 0–4, b = 0–2, and c = 1 or 2), which he obtained in preparative yields. Other workers have carried out similar transformations[242,243].

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CHEMISTRY OF NATURAL ALIPHATIC ACIDS CONTAINING A CONJUGATED SYSTEM OF DOUBLE BONDS

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1. INTRODUCTION

Until recently only a very small number of aliphatic acids containing a conjugated system of double bonds had been found in Nature. These acids had been isolated in individual cases from plant lipids, and were regarded in oil and fat chemistry as fairly rare exceptions. The view was even expressed that they might have been formed in the course of isolation, by the isomerisation of unconjugated polyenoic acids. However, several new representatives of this class of compounds have been discovered in recent years, and aliphatic acids containing conjugated double bonds have been shown to be present in the lipids from plants of a great variety of families and species. Sixteen natural conjugated polyenoic aliphatic acids are now known, and the number of natural sources for acids of this type is continually being extended.

Conjugated polyenoic acids form the basis of many long-established film-forming materials. The paint and varnish industry has hitherto made widespread using of drying oils, in which conjugated polyenoic acids either are present in the sodium form (tung oil) or have been formed, as a result of preliminary treatment, from unconjugated polyenoic acids present in linseed or other vegetable oil. In contrast to oils containing unconjugated polyenoic acids, the triglycerides of conjugated acids give valuable varnishes, which dry more rapidly and are more stable to the action of moisture and alkalis.

2. GENERAL PROPERTIES AND METHODS OF ESTABLISHING STRUCTURE

The C_{18} conjugated polyenoic acids most frequently encountered in Nature are colourless crystalline solids. Naturally occurring acids of this type containing a smaller number of carbon atoms in the chain melt below room temperature. They all dissolve well in polar organic solvents, and less well in non-polar solvents.

Polyenoic acids containing *cis*-ethylenic bonds readily isomerise into all-*trans*-isomers under the influence of light and especially in the presence of traces of iodine, sulphur, nitrogen dioxide, and other catalysts.

As a result of the presence of a chromophoric group, conjugated polyenoic acids are able to absorb ultraviolet radiation. Examination of the ultraviolet spectra of stereoisomeric dienoic acids has shown that *trans-trans*-isomers absorb at shorter wavelengths than do *cis-trans*- and *cis-cis*-isomers, the intensity of the absorption maxima diminishing in this sequence. Thus the ultraviolet spectra of the stereoisomeric octadeca-9,11- and -10,12-dienoic acids contain a single maximum at 230, 232, and 234 nm respectively for the *trans-trans*-, *trans-cis*-, and *cis-cis*-isomers[1]. The variation in the position of the absorption maximum and in its intensity is less marked in the spectra of the deca-2,4-dienoic acids, owing to conjugation of the diene group with the carboxyl, but is sufficient to distinguish them[2]. Variations in the ultraviolet spectra are still more marked among the stereoisomers of conjugated trienoic acids, since their spectra contain three absorption maxima (Table 1).

Infrared spectroscopy has an important place in establishing the structure of conjugated polyenoic aliphatic acids. Alkenes of the type RCH:CHR′ are characterised by an intense band at 950–1100 cm^{-1}, due to deformation vibrations

TABLE 1. Ultraviolet spectra of C_{18} conjugated trienoic acids (λ_{max}, nm).

Conjugation	Positions 8, 10, 12	Positions 9, 11, 13	Ref.
cis-trans-cis	265, 275, 287	264, 274, 285	3, 4, 5
		265, 275, 287	5
cis-cis-trans	not known	(264), 271, (279)*	4
cis-trans-trans	261, 271, 232	261, 271, 281	6, 3
trans-trans-cis	262, 272, 283	262, 272, 283	7, 8
trans-trans-trans	259, 269, 280	260, 269, 281	7, 6
	259, 269, 279	259, 268, 279	3, 5

* Values in parentheses relate to an unpurified specimen.

of the *trans*-ethylenic hydrogen atoms, or a band in the range 620–730 cm^{-1} with *cis*-alkenes[9,10], as well as a low-intensity peak in the range 1600–1660 cm^{-1}. These bands may occupy different positions within the above ranges depending on the nature of the substituents R and R′. In particular, the spectrum of elaidic acid contains a band at 968 cm^{-1}, whereas such absorption is absent with oleic acid[11]. The first systematic investigation of the infrared spectra of stereoisomeric conjugated dienoic acids was made on the methyl deca-2,4-dienoates and the corresponding deca-2,4-dienols[2]. Their spectra differed slightly in the position of weak bands in the region of C=C stretching vibrations (~1600 cm^{-1}) but differed very sharply in the region of deformation vibrations undergone by C–H bonds adjacent to ethylenic carbon atoms (940–1100 cm^{-1}) (Table 2).

Table 2 shows that the infrared spectra of the *trans-trans*-isomer contain only one intense band at 950–1010 cm^{-1}, whereas those of all the *trans-cis*-isomers contain also a somewhat less intense band at 950–970 cm^{-1}. The peaks at 1600–1660 cm^{-1} are considerably less intense and are less distinctive of the isomeric dienes.

The infrared spectra of nona-3,5-dienoic[11,12] and trideca-3,5-dienoic[13] acids also exhibit the presence of two bands (at 950 and 980 cm^{-1}) with the *trans-cis*-isomers and of one band in the same range with the *trans-trans*-isomers.

Analogous regularities are observed also in the infrared spectra of conjugated trienoic and tetraenoic acids. Without exception, all the all-*trans*-acids exhibit only one intense band, in the range 1000–940 cm^{-1}. Their isomers, containing both *cis*- and *trans*-ethylenic bonds, usually display two intense peaks in the same range of the infrared spectra (see examples in Table 3) and a band in the range 650–750 cm^{-1} which is characteristic of a *cis*-ethylenic bond. On the photochemical isomerisation of *cis-trans*-isomers into all-*trans*-forms, the peak at 960 cm^{-1} disappears, while the band at 1000 cm^{-1} shifts to 970 cm^{-1}. Thus a qualitative assessment of the character of the infrared spectra of conjugated polyenoic acids indicates whether they have an all-*cis*-, an all-*trans*-, or a *cis-trans*-configuration.

The relative proportions of *cis*- and *trans*-ethylenic bonds in conjugated polyenoic acids can be determined by measuring the intensity of the band in the range 970–1000 cm^{-1}, which is characteristic of non-planar deformation vibrations of *trans*-hydrogen atoms adjacent to double bonds. This parameter was found to be directly proportional to the number of *trans*-ethylenic bonds in a polyene chain, and is a multiple of the intensity of the corresponding band (968 cm^{-1}) in the spectrum of elaidic acid (provided that measurements are made on the same instrument)[11] (Table 3).

TABLE 2. Characteristic frequencies of infrared absorption bands due to ethylenic bonds in isomeric nona-2,4-dienols and methyl deca-2,4-dienoates.[2]

Configuration of 2,4-diene system	2,4-Dienols			Methyl deca-2,4-dienoates		
	stretching vibrations		deformation vibrations	stretching vibrations		deformation vibrations
	C=C (1)	C=C (2)	(CH=CH)$_2$	C=C (1)	C=C (2)	(CH=CH)$_2$
trans-trans	1660	1626	986, —	1647	1618	1001, —
trans-cis	1655	1616	983, 948	1639	1607	996, 969
cis-trans	1652	1609	984, 952	1640	1602	1002, 963
cis-cis	1651	1601	985*, 951*	1634	1592	1002*, 963*

* The presence of these bands is explained by contamination with *trans*-isomers owing to the ready isomerisation of the *cis-cis*-form.

TABLE 3. Extinction coefficients K of C_{18} aliphatic acids $CH_3[CH_2]_l[CH{:}CH]_m[CH_2]_kCOOH$ in the range 900–1000 cm^{-1} of the infrared spectra.[11]

n	m	k	Configuration	ν_{max}, cm^{-1}	K
7	1	7	*cis*	968	0.124
7	1	7	*trans*	968	0.601
5	2	7	*trans-trans*	987	1.270
5	2	7	*cis-trans*	950	0.501
				985	0.453
4	2	8	*trans-trans*	987	1.250
4	2	8	*cis-trans*	950	0.565
				985	0.485
3	3	7	*trans-trans-trans*	994	1.955
3	3	7	*cis-trans-trans*	965	0.416
				992	1.425
1	4	7	*all-trans*	998	2.80
1	4	7	*2-cis and 2-trans*	952	0.483
				994	1.55

Besides physicochemical methods for investigating the structure of conjugated polyenoic acids, use is made also of such classical chemical methods as catalytic hydrogenation, halogenation, and oxidative cleavage. The last of these methods (ozonolysis and the permanganate–periodate method) enables the position of a polyene group in an aliphatic chain to be determined, since it involves formation of monocarboxylic and dicarboxylic acids each containing one extra carbon atom compared with the radicals attached to the double bonds:

$$RCH{=}CH{-}CH{=}CH[CH_2]_nCOOH \xrightarrow{[O]} RCOOH + HOOC[CH_2]_nCOOH.$$

The above methods make it possible to establish the structure of the acids and to determine the ratio of *cis*- and *trans*-ethylenic bonds. However, the sequence of the double bonds cannot be determined by these methods. In most cases this question can be answered by studying the products of the diene condensation of the polyenoic acids with maleic anhydride. Among conjugated dienes, it is usually only aliphatic *trans-trans*-dienes which undergo the Diels–Alder reaction. The *cis-trans*-dienes either do not react at all with maleic anhydride or else react under severe conditions in a manner differing from that of diene synthesis[14,15]. The formation of adducts with maleic anhydride may serve as evidence of the presence of a conjugated *trans-trans*-diene group in a polyene compound, and has been used in establishing the configuration of naturally occurring conjugated trienoic acids. In this case the configuration of the third ethylenic bond in the acid, which remains unchanged in the aliphatic chain of the adduct, can be confirmed by infrared spectroscopy: the methyl esters of adducts containing an exocyclic *trans*-ethylenic bond exhibit an intense band in the range 1000–950 cm^{-1}, whereas this band is absent with adducts containing a *cis*-bond[16,17].

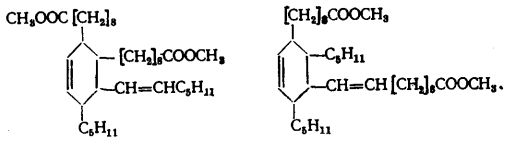
All natural polyenoic acids containing conjugated bonds are distinguished by considerable instability. They are extremely readily oxidised in the air, to form various hydroperoxides, which in turn initiate polymerisation processes[18]. Acids containing one or more *cis*-ethylenic bonds are oxidised considerably more readily than are all-*trans*-isomers[19] (see Table 4).

TABLE 4. Rate of oxidation of octadecatrienoic acids at 40°.[20]

Acid	Configuration of unsaturated system	Molar O_2/acid ratio after 100 min
α-Elaeostearic	*cis-trans-trans*, conjugated	2.68
β-Elaeostearic	*trans-trans-trans*, conjugated	1.02
Linolenic	*cis-cis-cis*, unconjugated	0.52

The presence of traces of water, irradiation, heating, and other factors considerably accelerate the polymerisation of these compounds[18,21]. These facts are of fundamental importance in the application of derivatives of polyenoic acids in the manufacture of varnishes.

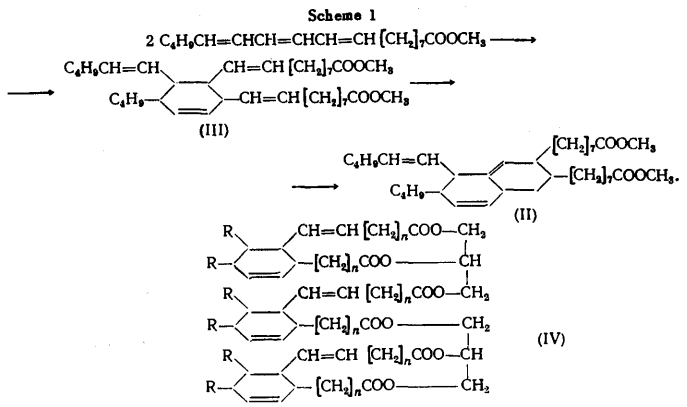
The thermal polymerisation (in the absence of oxygen) of compounds containing different numbers of double bonds, of different degrees of conjugation, and differing in configuration also occurs at different rates. Thus the thermal polymerisation of conjugated *trans-trans*- and *trans-cis*- and of unconjugated *cis-cis*-dienoic C_{18} acids takes place at relative rates of 40 : 7 : 1.[21] Their polymerisation probably has a bimolecular mechanism of diene condensation[22], but intramolecular cyclic structures may be formed. It has been discovered that unconjugated and conjugated dienoic acids give identical dimerisation products, which indicates that the polymerisation of unconjugated polyenoic acids involves their conversion into conjugated acids[22]. The most detailed investigation that has now been made is of the structure of the products formed by the polymerisation of methyl octadeca-*trans*-10, *trans*-12-dienoate, which are obtained when it is heated at 250° for 5 h. The results of nuclear magnetic resonance, mass, and infrared spectroscopy and of ozonolysis have shown that the main products of this reaction are 3,4,5,6-tetrasubstituted cyclohexene dimers of type (I), having an αβ-ethylenic bond in a side-chain[23].



(Ia) (Ib)

Under these conditions trienoic esters probably form dicyclic dimers of type (II) or monocyclic dimers having the structure (III) (see Scheme 1)[22,24], whereas their triglycerides yield structures of type (IV). The dimeric molecules may undergo further condensation by interaction at isolated double bonds with the conjugated bonds of the monomers[25].

Scheme 1



3. DIENOIC ACIDS

Stillingic Acid

The only C_{10} dienoic acid which has been found in Nature is deca-2,4-dienoic (stillingic) acid, which has been isolated from the seed oil of *Sapium sebiferum* (the Chinese tallow tree) and *S. discolor*. The content of stillingic acid in the oils of these seeds does not exceed 4–5%. A 2,4-dienoic acid was first detected in these sources from the characteristic absorption maximum in the ultraviolet spectrum (260 nm);[26,27] soon after this it was isolated and characterised, and its structure was established[28-31].

Stillingic acid oxidises in the air even at ordinary temperatures. Exhaustive hydrogenation yields n-decanoic acid. The products of destructive oxidation of its methyl ester are found to include n-hexanoic acid, the formation of which proves that the ethylenic bonds in the dienoic acid are located in the 2- and 4-positions[28]. Partial hydrogenation of methyl stillingate gave mainly the dec-3-enoic ester, together with small quantities of the dec-2-enoate and dec-4-enoate. Reduction of methyl stillingate with lithium tetrahydroaluminate gave deca-2,4-dienol, which had an ultraviolet absorption maximum at 231 nm (ε = 22 500), and on alkaline isomerisation a mixture of deca-4,6- and -5,7-dienoic acids was formed[31].

Since the configuration of the diene system of stillingic acid could not be established in the original investigation[28-31], nor could it be satisfactorily analysed or its crystalline derivatives characterised, a further detailed study was made of this acid[2]. In order to establish its configuration, all four possible geometric isomers of deca-2,4-dienoic acid were synthesised (see Section 5). The naturally occurring acid and the synthetic *trans*-2,*cis*-4-isomer had the same ultraviolet and infrared spectra and gave identical *p*-bromophenacyl esters and *S*-benzylthiouronium salts, so that the *trans*-2,*cis*-4-configuration was proposed for stillingic acid.

Dodeca-2,4-dienoic Acid

A dodeca-2,4-dienoic acid has been detected in the seed oil from *Sebastiana lingustrina* (Euphorbiaceae family), a plant growing in North America[32]. Two moles of hydrogen are absorbed on hydrogenation, with the formation of lauric acid. The position of the absorption maximum in the ultraviolet spectra of the methyl ester (268 nm) and of the acid (260 nm, ε = 33 400) is characteristic of 2,4-dienoic acids[2,33]. The configuration of the diene grouping in this acid has not yet been settled. From the position of the ultraviolet absorption maximum for methyl dodeca-2,4-dienoate, the acid may be supposed to be the *trans*-2,*cis*-4-isomer, but the position of the maximum in the ultraviolet spectrum of the acid itself and the extinction are characteristic of acids having a *trans-trans*-configuration.

Octadeca-*trans*-10,*trans*-12-dienoic Acid

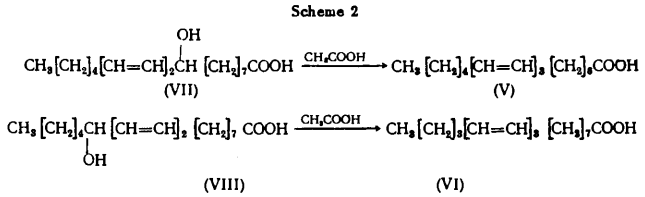
A positional isomer of this acid having an unconjugated system of double bonds — linoleic acid — is the most widespread "essential" fatty acid in Nature. In spite of this, no isomer of it having conjugated bonds was known until recently. There were only isolated references to the presence of such an isomer in lipids from the plant *Catalpa bignonioides* and *Chilopsis linearis*[5,8,34] and in some other

plants[35,36]. The seeds of *Chilopsis linearis*, a small ornamental tree from the Southern USA, contain a trienoic as well as the dienoic acid. Careful low-temperature recrystallisation of the mixture of these acids obtained by saponifying the seed oil resulted in the isolation of 9% of a dienoic acid having m.p. = 55–56° and λ_{max} = 232 nm (ϵ = 29 200), with infrared absorption bands at 985 and 930 cm^{-1}.[37] Catalytic hydrogenation of this acid yielded strearic acid. The location of the diene grouping at the 10,12-positions was proved by oxidative cleavage. Although only one intense absorption band is usually oserved in the range 900–1000 cm^{-1} in the infrared spectra of conjugated *trans*--*trans*-dienes, this configuration was assigned to the octadeca-10,12-dienoic acid which was isolated, since the latter formed an adduct with maleic anhydride (m.p. 102–103°) which gave no melting-point depression on fusion with a known specimen[38]. This acid had been obtained previously by the dehydration and isomerisation of ricinoleic acid isolated from castor oil[39], and by the alkaline isomerisation of linoleic acid[1].

cis-trans-9-Hydroxyoctadeca-10,12-dienoic and -13-Hydroxyoctadeca-9,11-dienoic Acids

The oil from the plants *Tragopogon porrifolius* (Compositae family) is known as a source of saturated epoxy--acids[40]. It has recently been found to contain a polyene fraction of unusual composition, in amount not exceeding 4–5% according to ultraviolet spectral data[7]. After separation of unsaponifiable products, conjugated dienoic acids having an ultraviolet absorption maximum at 233 nm and infrared absorption bands at 3580, 945, and 980 cm^{-1} were isolated. The first band indicated the presence of a hydroxyl, and the latter bands the presence of a *cis-trans*--diene grouping. The mixture of dienoic acids isolated was subjected to oxidative cleavage by the permanganate–periodate method, which showed the presence of diene groupings in the 9,11- and 10,12-positions. On boiling with glacial acetic acid the mixture of acids formed a mixture of octadeca-8,10,12- and -9,11,13-trienoic acids — (V) and (VI), see Scheme 2.

Scheme 2



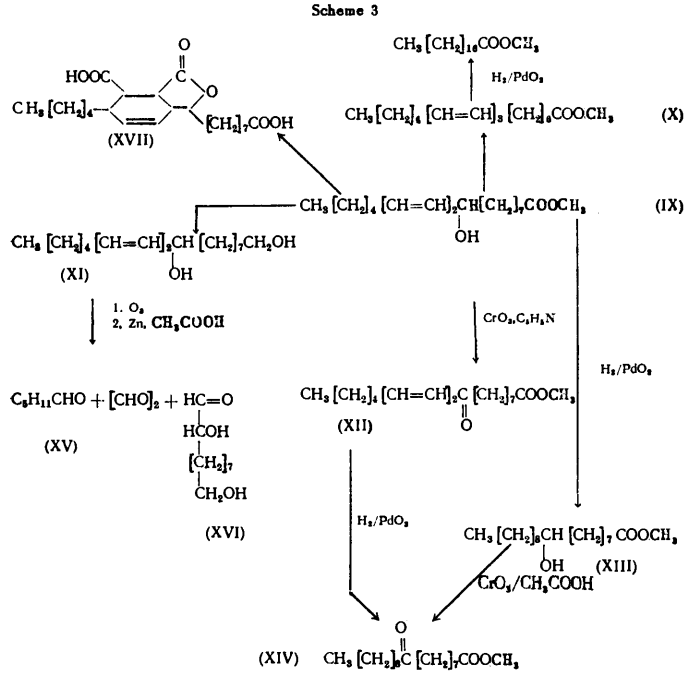
Catalytic hydrogenation of this mixture of trienoic acids yielded stearic acid, whereas oxidative cleavage yielded valeric, suberic, and azelaic acids. The ease of dehydration indicated that the hydroxy-groups in the original acids occupied an allylic position with respect to the diene grouping. This suggestion was confirmed by study of the hydrogenation products obtained from the mixture of hydroxy-acids (VII) and (VIII), which comprised a mixture of monohydroxystearic acids of m.p. 65–66°. The location of the hydroxyls in the latter acids (at positions 9 and 13) was proved by oxidative cleavage to the corresponding dicarboxylic and monocarboxylic acids.

On the basis of the infrared spectra of the natural acids and their esters, a *cis-trans*-configuration was assigned to them. However, spectral data do not permit the possibility to be excluded that only one of the dienoic acids may possess a *cis-trans*-configuration, while the other may have a *cis*--*cis*- or *trans-trans*-configuration. The position of the *cis*- and *trans*-ethylenic bonds in the molecules of the natural acids remains undetermined.

Dimorphecolic Acid

In order to find new sources for valuable industrial oils, a study was made of the composition of lipids from a large group of plants of the Compositae family[41]. Several of them, in particular the oil from *Dimorphotheca aurantiaca* (or *D. sinuata*), were found to contain a considerable quantity (up to 50%) of a conjugated dienoic acid as well as epoxy--acids. Mild saponification of this oil gave a dienoic acid, sensitive to alkali under more severe conditions, which was purified by countercurrent distribution as the methyl ester in an acetonitrile–hexane system. The methyl ester (IX) exhibited optical activity, absorbed in the ultraviolet at 231 nm, and possessed infrared absorption bands corresponding to a conjugated *trans-trans*-diene (992 cm^{-1}) and a hydroxy-group. On boiling under conditions of acetolysis of the epoxy-compounds, the dimorphecolic ester was converted into a trienoic acid (X) containing no hydroxyl, which was reduced catalytically to stearic acid. Lithium tetrahydroaluminate reduction of the ester (IX) to the dienediol (XI) also confirmed the absence of an epoxy-group in the ester molecule (IX). Oxidation with chromium trioxide yielded the dienone (XII), which had a maximum in the ultraviolet spectrum at 275 nm, corresponding to $\alpha\beta$- and $\gamma\delta$-unsaturated ketones. The location of the hydroxyl in dimorphecolic acid was established by comparing the products obtained by reducing the keto-ester (XII) and oxidising the hydroxy-ester (XIII) with the identical synthetic keto-ester (XIV). Furthermore, ozonolysis of the dienediol (XI) yielded glyoxal and the aldehydes (XV) and (XVI), identified as their 2,4-dinitrophenylhydrazones. On the other hand, dimorphecolic ester (IX) reacts with maleic anhydride to form a lactone (XVII), which confirms the *trans-trans*--configuration of the 10,12-diene grouping in dimorphecolic acid[42] (see Scheme 3).

Scheme 3



Methods were later developed, to meet the requirements of the paint and varnish industry, for isolating dimorphecolic acid as its methyl ester from the triglycerides in *Dimorphotheca* oil, these involving transesterification of the oils in methanolic solution on a hydroxylated ion-exchange resin [43,44].

Dimorphecolic acid has subsequently been found in the oils from 29 species of plants, in which it constitutes 34–75% of the total acids [45]. There is indirect evidence of the presence in some of these specimens of another isomer of dimorphecolic acid, with the hydroxyl in position 13 and the diene grouping in positions 8 and 10. [46]

The ready dehydration of dimorphecolic acid makes it a very probable biological precursor of calendic acid (see below), which was found to accompany the former in most of the plants investigated [45].

TABLE 5. Natural sources of α-elaeostearic acid.

Plant	% of total acids	Ref.
Aleurites cordata	74	50
» *fordii*	77—86	51—53
» *montana*	71—82	54
» *trisperma*	51—67	55,56
Garcia nutans	93—95	57,58
Licania rigida	16—17	59
Mallotus phillipinensis	38	60
Parinarium campestre	49	61
» *corymbosum*	13—15	61
» *laurinum*	30—34	62
» *macrophyllum*	30—32	53,63,64
» *scherbroense*	32—37	65
Ricinodendron africanum	49—53	66
Telfaira occidentalis	19	67
Catalpa bignonioides	31	68
Momordica charantia	57	69—71

4. TRIENOIC AND TETRAENOIC ACIDS

Since trienoic acids may differ from one another both in the position of the triene system in the aliphatic chain and in the configuration of the double bonds, the number of possible isomers is very large. In spite of this, only eight naturally occurring acids of this type are known at the present time. They all oxidise and polymerise readily in air even at room temperature.

α-Elaeostearic Acid

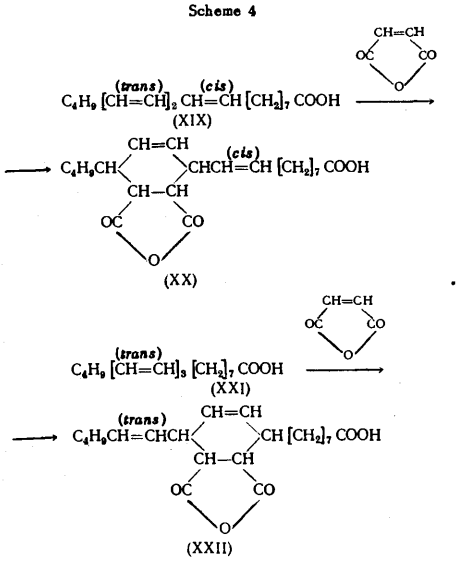
α-Elaeostearic acid is the most widely occurring conjugated trienoic acid in Nature (Table 5). The best-known source of the acid is tung oil, from which it was isolated as long ago as 1875. [47,48] The formula $C_{18}H_{30}O_2$ was established for α-elaeostearic acid in 1902, and a higher-melting β-form was obtained for the first time [49]. Pure α-elaeostearic acid, isolated from tung oil and purified by low-temperature recrystallisation from alcohol, melts at 48°. [3,4] Under the influence of ultraviolet radiation in the presence of traces of iodine or sulphur, it is readily converted into β-elaeostearic acid melting at 72°. [4] Both acids form adducts with maleic anhydride on heating in benzene, these melting at 62.5° and 77° respectively [72], and bromination yields hexabromides melting at 139–141° and 157°. [73,74] α-Elaeostearic acid forms a crystalline *p*-phenylphenacyl ester melting at 63–64°. [70] On catalytic hydrogenation both acids give stearic acid, equimolecular mixtures of isomeric octadecenoic acids being formed as intermediate products [75–77]. The action of hydrazine on α- and β-elaeostearic acids involves reduction firstly of terminal units in the polyene chain, with the formation of the 11-enoic and the 9,11- or 11,13-dienoic acids, a *cis*-ethylenic bond in the polyene system being reduced rather more rapidly [78] [than the corresponding *trans*-bond (Ed. of Translation)].

The ultraviolet spectra of α- and β-elaeostearic acids show absorption maxima characteristic of trienes — at 261, 271, and 281 nm (ε = 36 000, 47 000, and 38 000 respectively); and at 259, 268, and 279 nm (47 000, 61 000, and 49 000). [3]

At 0° both forms add on two molecules of bromine to form tetrabromides, so for a long time they were regarded as dienoic acids, to which different cyclic structures were attributed. It was later suggested that the ethylenic bonds in the acids were conjugated [79], and valeraldehyde, valeric acid, and azelaic acid were detected in the hydrolysis products of their ozonides [80]. Together with the facts that on catalytic hydrogenation 1 mole of elaeostearic acid absorbed 3 moles of hydrogen and that its molecular refraction was too high to correspond to a diene, this enabled the true structure of the acid to be established [81,82]. The structure of elaeostearic acid was confirmed also by the 60% yield of glyoxal obtained on hydrolysis of its ozonide, while no succinic or malonic acid was detected [83]. Hexabromostearic acid was subsequently obtained [73,74] by bromination with ultraviolet irradiation and heating. Thus the structural formula of elaeostearic acid was finally established by 1930, but its configuration remained unelucidated.

The original investigations of the structure of the adducts formed by α- and β-elaeostearic acids with maleic anhydride did not provide the right answer to this question [72,81–87]. The location of the cyclohexene ring in the aliphatic chain of the adducts was merely established, and an adduct having the structure (XX) was shown to be formed from α-elaeostearic acid (XIX), since azelaic acid was detected among the products of the oxidative cleavage of this adduct (Scheme 4).

Scheme 4



The structure of the adduct formed by maleic anhydride with β-elaeostearic acid was established (XXII) in a similar manner[72].

After it had been ascertained that maleic anhydride undergoes diene condensation only with *trans-trans*-diene groups[14], several authors suggested that α-elaeostearic acid had the *cis*-9,*trans*-11,*trans*-13-configuration (XIX), while β-elaeostearic acid was the all-*trans*-isomer (XXI).[11,16,17,88] These configurations were subsequently confirmed by examination of the infrared spectra. Thus α-elaeostearic acid (XIX) exhibits intense absorption bands in the region of out-of-plane deformation vibrations of *trans*-ethylenic hydrogen atoms at 992 and 965 cm^{-1}, with intensity coefficients K of 1.43 and 0.416 respectively; the infrared spectrum of the β-isomer (XXI) has an absorption band at 994 cm^{-1} with K = 1.96, threefold the intensity of the corresponding band for elaidic acid at 968 cm^{-1}. From this it was concluded that the β-isomer had an all-*trans*-configuration. From the same considerations the α-acid (XIX) was assumed to contain one *cis*-ethylenic bond[11]. In this case one of three configurations — *trans-trans-cis*, *cis-trans-trans*, or *trans-cis-trans* — was possible, of which the second was the most probable, since α-elaeostearic acid formed only an adduct having the structure (XX). Furthermore, the infrared spectrum of the methyl ester of the adduct (XXII), in contrast to the adduct (XX), contained an absorption band in the range 1000–950 cm^{-1}, indicating that the ethylenic bond in the aliphatic chain of the adduct (XXII) had the *trans*-configuration[16,17].

The structure (XIX) for α-elaeostearic acid was finally proved by synthesis (see Section 5).[4,89]

Punicic Acid

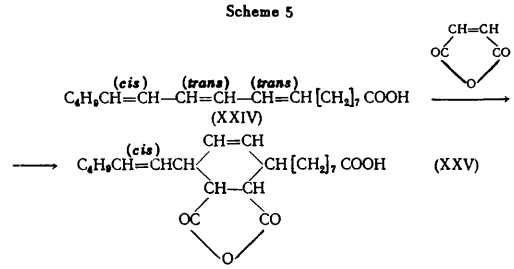
Punicic acid was first isolated from the seed oil of the pomegranate (*Punica granatum*)[90], where it forms 72% of the total aliphatic acids. It is met also in the plants *Momordica balsamina*[72], *Trichosanthes anguina* (43%)[70], *Ecballium elaterum* (Cucurbitaceae) (22%)[71], etc. The ultraviolet spectrum of punicic acid (m.p. = 42°) contains three maxima, at 265.5, 275 (ε = 47 800), and 287 nm. The infrared spectrum contains absorption bands at 988 and 937 cm^{-1} (K = 0.63 and 0.7 respectively)[91]. On the basis of these data it was suggested — erroneously, as appeared later — that punicic acid had a *cis-cis-trans*-configuration[91,92]. The acid does not form an adduct with maleic anhydride, and on ultraviolet irradiation is converted into β-elaeostearic acid (XXI).[16]

At roughly the same time an acid melting at 35–35.5°, which was termed "trichosanic acid", was isolated from the oil of the Japanese snake gourd (*Trichosanthes cucumeroides*)[90]. Its ultraviolet and infrared spectra were identical with those of punicic acid, and under the influence of ultraviolet radiation both acids isomerised into β-elaeostearic acid (XXI), so that trichosanic acid was assumed to be a third geometric isomer of α-elaeostearic acid (XIX). The presence of trichosanic acid in Japanese snake gourd[93,94], and also in the oil of the Indian snake gourd (*Trichosanthes anguina*)[94,95], was subsequently confirmed by other workers. In order finally to establish the structure of punicic and trichosanic acids, the synthesis was then undertaken of two isomeric octadecatrienoic acids by Scheme 10*b*. Comparison of natural and synthetic specimens showed that both punicic and trichosanic acids were octadeca-*cis*-9,*trans*-11,*cis*-13-trienoic acid (XXIII).

Catalpic Acid

Catalpic acid was isolated from the seed oil of the decorative plant *Catalpa ovata* (Bignoniaceae)[8], *C. speciosa*[71], and *Chilopsis linearis*[37,38]. α-Elaeostearic acid (XIX) had previously been found in the seed oil of various *Catalpa* species[68]. Pure catalpic acid was still less stable than punicic acid (XXIII) or α-elaeostearic acid. It melts at 31–32°, and oxidised rapidly in the air, being converted into a non-crystalline solid mass even at room temperature. Its ultraviolet spectrum contains absorption maxima at 262, 272 (ε = 49 300), and 283 nm, which are characteristic of conjugated trienes[8]. The character of these maxima, together with the results of elementary analysis and hydrogenation, showed that catalpic acid, like elaeostearic and punicic acids, is an octadecatrienoic acid containing a conjugated system of ethylenic bonds.

Scheme 5



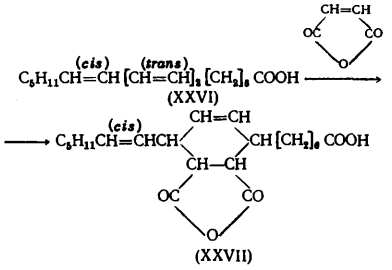
Gas–liquid chromatography of the products obtained by the oxidative cleavage of catalpic acid has shown that the triene grouping occupies the 9–13 positions. This is confirmed also by the isomerisation of catalpic acid (XXIV) into β-elaeostearic acid (XXI) on ultraviolet irradiation in the presence of iodine. The infrared spectrum of catalpic acid (XXIV) resembles that of α-elaeostearic acid, containing in particular bands at 987 and 957 cm^{-1} of the same relative intensities as with the latter acid. Catalpic acid (XXIV) readily forms an adduct (XXV) with maleic anhydride (Scheme 5), melting at 72.5–73.5° and possessing no infrared absorption band in the range 950–1000 cm^{-1}, so that the double bond in the aliphatic chain of the adduct has the *cis*-configuration. Of the eight possible isomers of octadeca-9,11,13-trienoic acid, only two — the *trans-trans-cis*- and *cis-trans-trans*-isomers — are able to form such an adduct. Since the latter isomer is α-elaeostearic acid (XIX), only the structure (XXIV) is available for catalpic acid. A complete synthesis of catalpic acid has recently been achieved by means of the Wittig reaction (Scheme 13).

Calendic Acid

Calendic acid has been isolated from the seed oil of *Calendula officinalis* (Compositae)[5]. Its isomer having the *trans-trans-trans*-configuration (β-calendic acid) is not present in this oil, but is obtained from it as a result of the isomerisation of calendic acid in the course of isolation[7]. Conjugated trienoic acids, in particular octadeca-8,10,12-trienoic acid, have been detected in other plants — *Calendula arvensis*, *Osteospermum*, *Chrysanthemoides* — which are closely related to *Calendula*[45,96]. Calendic acid (XXVI) (m.p. 40–40.5°) was purified by low-temperature recrystallisation from acetone, and elementary analysis showed it to be an octadecatrienoic acid. On catalytic hydrogenation, α-calendic acid absorbs three molecules of hydrogen to form stearic acid. Oxidative cleavage of calendic acid results in rupture of the bonds in the positions 8–13. The

infrared spectrum of calendic acid contains absorption bands at 990 and 955 cm^{-1}, which suggests the presence of conjugated *cis*- and *trans*-ethylenic bonds. A similar conclusion follows also from an examination of the positions of its ultraviolet absorption maxima (at 262, 272, and 283 nm). Calendic acid reacts readily with maleic anhydride (Scheme 6) to form an adduct of m.p. 73–74°, whose infrared spectrum does not contain the absorption bands in the range 1000–950 cm^{-1} which are characteristic of the spectra of adducts containing an exocyclic *trans*-ethylenic bond. Oxidative cleavage of the adduct by the permanganate–periodate method yields only one monocarboxylic acid — n-hexanoic acid — so that the adduct has the formula (XXVII). Thus the *trans*-8,*trans*-10,-*cis*-12-configuration has been established for calendic acid.

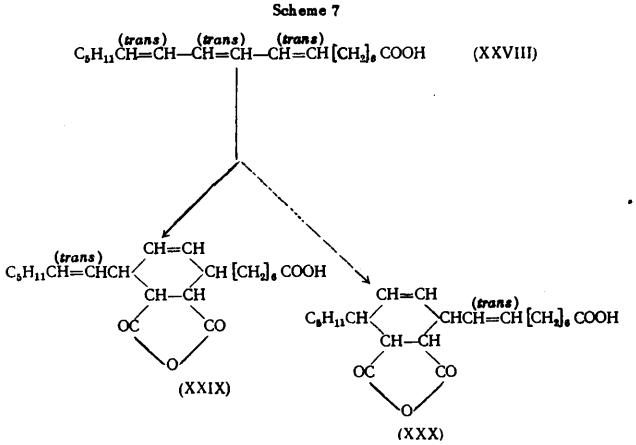
Scheme 6



(XXVII)

When calendic acid is treated with iodine in pentane and on ultraviolet irradiation, it passes into β-calendic acid (XXVIII), melting at 77–78° and exhibiting an intense infrared peak at 990 cm^{-1}.[11,17] A 950 cm^{-1} band is also present in the infrared spectrum of the photochemical isomerisation product, but its intensity is considerably less than in the infrared spectrum of the original *trans*-*trans*-*cis*-isomer (XXVI). The ultraviolet absorption maxima of β-calendic acid (XXVIII) are displaced to shorter wavelengths in comparison with natural calendic acid (XXVI) (258, 268, and 280 nm compared with 262, 272, and 283 nm)[7] (see Scheme 7). The infrared spectrum of the adduct formed by β-calendic acid with maleic anhydride (m.p. 70–71°) contains an absorption band at 963 cm^{-1}, which is characteristic of a *trans*-exocyclic double bond. Permanganate–periodate cleavage of this adduct gave both n-hexanoic and suberic acids, so that the adduct melting at 70–71° was a mixture of the isomers (XXIX) and (XXX). Further confirmation of the structure of calendic acid has been provided by its complete synthesis (Scheme 13).

Scheme 7



(XXIX) (XXX)

Jacarandic Acid

Another stereoisomer of calendic acid (XXVI) — jacarandic acid (XXXI), found in the seed oils of *Jacaranda mimosifolia* (Bignoniaceae) and *Dimorphotheca aurantiaca*[5,58] — is stereochemically analogous to punicic acid (XXIII). These two acids are very similar in spectral characteristics and in melting points (43.5–44°).

Jacarandic acid oxidises very readily in the air, and is extremely unstable at temperatures above -20°. Catalytic hydrogenation and oxidative cleavage have shown it to be a C_{18} acid having a triene grouping in the positions 8–12 of the aliphatic chain[5,31]. Furthermore, this acid does not form an adduct with maleic anhydride, and on ultraviolet irradiation passes into a higher-melting form which proves to be identical with β-calendic acid (XXVIII). All these results indicate the absence of a *trans*-*trans*-diene grouping and the presence of at least one *cis*-ethylenic bond in jacarandic acid. Structures containing *cis*-*trans*-*trans*-, *trans*-*trans*-*cis*-, or *trans*-*trans*-*trans*-triene systems are therefore excluded. The presence in the infrared spectrum of jacarandic acid of an intense band at 982 cm^{-1} (together with a band at 929 cm^{-1}), which is characteristic of a *trans*-ethylenic bond, also excludes a *cis*-*cis*-*cis*--configuration. The *cis*-*cis*-*trans*- and *trans*-*cis*-*cis*--structures were rejected on the grounds that the infrared and ultraviolet spectra of jacarandic acid (XXXI) and of synthetic octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid[4] differ fundamentally. In particular, the ultraviolet spectrum of the synthetic acid contains only one absorption maximum, at 271 nm, with inflections at 263 and 279 nm, whereas the spectrum of jacarandic acid is characterised by a triplet at 265, 275, and 287 nm. Of the two possible remaining structures — *cis*-*trans*-*cis* and *trans*-*cis*--*trans* — the latter is inconsistent with the fact that the intensity of the absorption band at 982 cm^{-1} in the infrared spectrum of jacarandic acid is close to the intensity of the corresponding band of elaidic acid.

$$C_5H_{11}\overset{(cis)}{C}H{=}CH{-}CH{=}\overset{(trans)}{C}H{-}CH{=}\overset{(cis)}{C}H[CH_2]_6COOH \quad (XXXI).$$

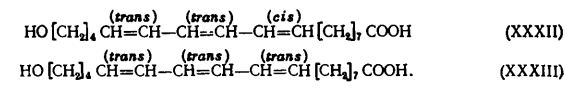
On the basis of all the above results, the structure (XXXI) has been put forward for jacarandic acid.

Kamlolenic Acid

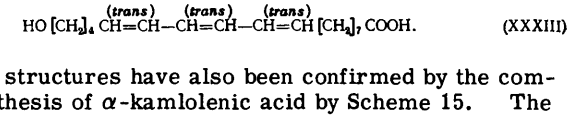
Kamlolenic acid is the main aliphatic acid in the oil from the kernels of *Mallotus philippinensis* (Euphorbiaceae), which has long been used as a purgative in popular medicine[97–100]. Like other trienoic acids, kamlolenic acid is known in the form of two geometric isomers[101]: the natural α-form melts at 77–78°; the β-isomer, formed from the α-form on ultraviolet irradiation, melts at 88–89°. Both forms yield crystalline methyl and *p*-bromophenacyl esters, acetyl derivatives, and 1-naphthylurethanes of the methyl esters[98,102]. On catalytic reduction both forms absorb three moles of hydrogen with the formation of 18-hydroxystearic acid[97–99,102]. The infrared spectra of the stereoisomeric kamlolenic acids and their methyl esters contain intense absorption bands at 3200 and 1060 cm^{-1}, due to a primary hydroxyl, while the spectrum of the α-isomer includes an intense doublet in the range 900–1000 cm^{-1}.[102]

Ozonolysis of methyl kamlolenate yielded the 9-oxononanoic ester, formed by cleavage of a 9,10-ethylenic bond[102]. Study of the infrared spectra of both isomeric forms, their acetyl derivatives, and the maleic anhydride

adducts led to the proposed structures (XXXII) for the α-form and (XXXIII) for the β-form [103-105].



(XXXII)

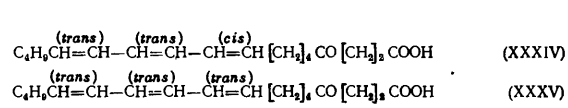


(XXXIII)

These structures have also been confirmed by the complete synthesis of α-kamlolenic acid by Scheme 15. The earlier suggestion that this compound was an unsaturated keto-acid [100] proved to be erroneous.

Licanic Acid

Licanic acid was first isolated in 1931, from the seed oil of the tropical tree *Licania rigida* [106]. In one of the early papers [107] the source of this acid was erroneously included in the family Couepia (*C. grandiflora*), on which basis it was given a different name, "couepic acid". Licanic acid was subsequently isolated also from other *Licania* species — *L. arbrorea* (*cacahunanche*) (Mexico) [108], *L. crassifolia* (East Indies) [109], *L. levenosa* (British Guiana) [110] — in the oils from which the content of this acid reaches 80% of the total acids. Furthermore, it accompanies eleaeostearic acid to form 35–70% of the seed oils from certain plants of the genus *Parinarium*, in particular *P. corymbosum* (*taritih*) [111], *P. glaberimum* (India) [19], *P. laurinum* (*makita*) (islands in the Pacific Ocean) [19], *P. macrophyllum* (*neou*) [62-64], and *P. sherbroense* (Africa) [65].



(XXXIV)

(XXXV)

Licanic acid melts at 63°. It forms a semicarbazone (m.p. 134–137° [112,113]) and an adduct with maleic anhydride (m.p. 79° [114]). Photochemical isomerisation of the natural α-licanic acid yields the higher-melting β-form (isolicanic acid, m.p. 99.5°). [16] Ultraviolet spectroscopy indicates that licanic acid contains a conjugated triene grouping. On catalytic reduction (after the absorption of three moles of hydrogen) 4-oxostearic acid is formed, and oxidation with dilute potassium permanganate solution at 0° yields n-valeric, 4-oxoazelaic, and oxalic acids. With maleic anhydride α-licanic acid forms an addition product in the 11,14-positions, since ozonolysis of the adduct yielded 4-oxoazelaic acid, while valeric acid was also detected in the case of β-licanic acid. On the basis of these results, and also the infrared spectra of α- and β-licanic acids and their adducts, the structures (XXXIV) and (XXXV) were suggested for these acids [16].

5-Acetoxymethyltetradeca-*trans*-2,*trans*-4,*trans*-6-trienoic Acid

Resinous substances in the leaves of the Australian tree *Eremophila oppositifolia* (Myoporaceae) contain, together with a large quantity of sesquiterpene alcohols, an unsaturated acetoxy-acid of m.p. 88–89° and empirical formula $C_{17}H_{26}O_4$. [115] The infrared spectrum of this acid contains bands corresponding to a conjugated triene grouping (980 and 965 cm^{-1}), an ester group (1743 cm^{-1}), and a carbonyl group (1686 cm^{-1}). Its ultraviolet spectrum contains a single maximum at 298 nm, characteristic of a triene system conjugated with a carboxyl.

On saponification of the acid (XXXVI) an intense band appears in the infrared spectrum at 3621 cm^{-1}, corresponding to an alcoholic hydroxyl. Catalytic reduction of the unsaturated acetoxy-acid (XXXVI) yields a mixture of 5-methyltetradecanoic acid (XXXVII) (hydrogenolysis product) and the saturated acetoxy-acid (XXXVIII) (see Scheme 8). The hydroxy-acid (XXXIX), obtained together with acetic acid on saponification of the natural acetoxy-acid (XXXVI), can be oxidised with manganese dioxide to the aldo-acid (XL), which indicates that its alcoholic hydroxyl occupies an allylic position [116]. The hydroxy-acid (XLI) is oxidised by chromic acid to a dicarboxylic acid (XLII), which on being heated with acetic anhydride yields 2-nonylcyclopentanone (XLIII), the formation of which proves that the side-chain in the natural acid (XXXVI) is attached to the $C_{(5)}$ atom.

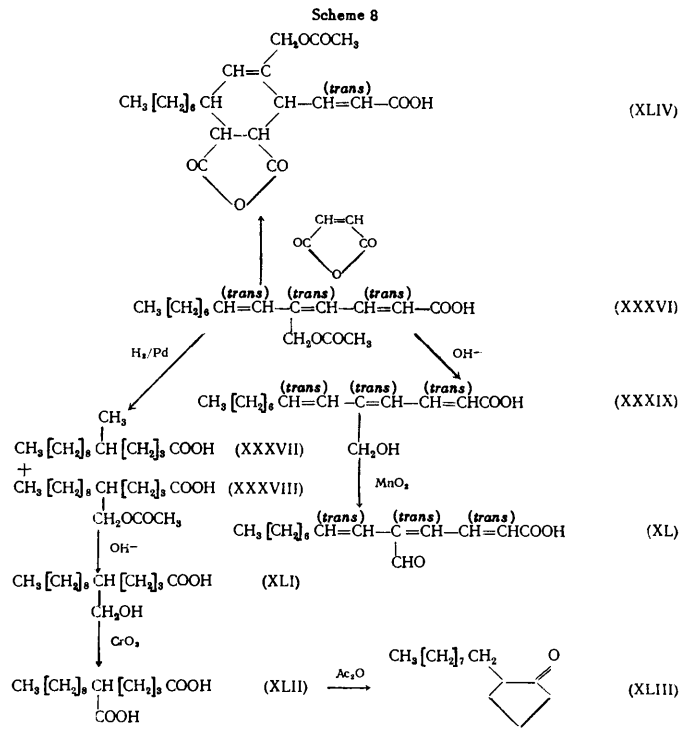
The position of the triene grouping in the aliphatic chain of the natural acid (XXXVI) was established by ozonolysis (n-octanal was found among the reaction products). This acid interacts with maleic anhydride to form an adduct (XLIV), whose infrared spectrum contains an absorption band at 965 cm^{-1}, which indicates that the exocyclic ethylenic bond in the adduct has the *trans*-configuration [16,17].

On the basis of these results the structure 5-acetoxymethyltetradeca-*trans*-2,*trans*-4,*trans*-6-trienoic acid (XXXVI) has been proposed for the naturally occurring acid.

Tetraenoic (Parinaric) Acids

Parinaric acid (XLV), first isolated from the oil obtained from *Parinarium laurinum* nuts (Table 6), was originally regarded as a trienoic acid, isomeric with elaeostearic acid (XIX). [117,119] Subsequently catalytic hydrogenation and determination of the iodine number established that four ethylenic bonds were present, and they were proved by ultraviolet

Scheme 8



(XLIV)

(XXXVI)

(XXXIX)

(XXXVII) + (XXXVIII)

(XL)

(XLI)

(XLII)

(XLIII)

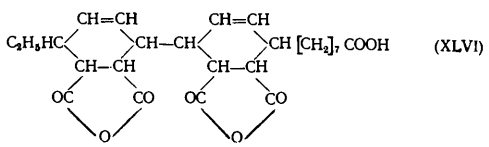
TABLE 6. Natural lipids containing parinaric acids.

Plant	Content in acid mixture, %	Ref.
Parinarium laurinum	46—56	117,118
Impatiens balsamina	—	121
» *fulva*	51	122
» *parviflora*	46	123,124
» *Royley*	40—50	122
» *holimetangre*	32	122
» *hortensis*	27	122
» *Sultanii*	—	122
» *Holstii*	13	122
Nyphaea alba	—	123
» *Iris*	—	123

spectroscopy [119,120] and oxidative cleavage [119] to be conjugated. Since propionic and azelaic acids were detected among the products of ozonolysis, the tetraene grouping in parinaric acid should occupy the positions 9–15 [118] (XLV).

Natural parinaric acid (the α-form), melting at 84–85°, can be converted by photochemical isomerisation into the β-form, having m.p. 95–96°, which was assigned the all-*trans*-configuration on the grounds that it formed an adduct with two molecules of maleic anhydride (XLVI). [124]

$$C_5H_9CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH\,[CH_2]_7\,COOH \qquad \text{(XLV)}$$



(XLVI)

The presence of four *trans*-ethylenic bonds in β-parinaric acid is further confirmed by the fact that the infrared band at 999 cm^{-1} due to such bonds is four times as intense as the 968 cm^{-1} band due to the *trans*-double bond in elaidic acid, and 40% more intense than the corresponding band in the infrared spectrum of α-elaeostearic acid (XXI). [11]

The infrared spectrum of α-parinaric acid also contains a band at 996 cm^{-1} due to a *trans*-ethylenic bond (together with a band at 952 cm^{-1}), the intensity of this band being half that of the corresponding band in the spectrum of the β-isomer, and double that of the band due to the *trans*-ethylenic bond in elaidic acid. It was therefore concluded that α-parinaric acid contains two *trans*-ethylenic bonds [11,124]. Since the α-isomer does not form an adduct with maleic anhydride, these bonds should be separated by one or two *cis*-ethylenic bonds. In such case α-parinaric acid may correspond to one of the three configurations — *cis-trans-cis-trans*, *trans-cis-trans-cis*, or *trans-cis-cis-trans* — but no data enabling a choice to be made among these configurations have yet been published†.

An investigation of the lipids from plants of the *Impatiens* genus revealed that the infrared spectrum of the seed oil was very similar to that of α-parinaric acid, but differed from the latter in the presence of an absorption band at 932 cm^{-1}. [124] An extremely unstable acid of m.p. 72–74°, termed impatienic acid and corresponding to parinaric acid in composition, was isolated by saponifying the oil in the cold and then rapidly recrystallising at low temperature. Its infrared spectrum was analogous to that of the original oil, but its ultraviolet spectrum was identical with that of α-parinaric acid (Table 7). When stored in a vacuum at 20° for a short while, impatienic acid changes into α-parinaric acid, the 932 cm^{-1} infrared band disappearing.

The problem of the configurations of parinaric and impatienic acids can probably be finally solved by means of the nuclear magnetic resonance spectra with appropriate synthetic models available.

5. SYNTHESES OF NATURALLY OCCURRING POLYENOIC ALIPHATIC ACIDS

In spite of the fact that conjugated polyenoic aliphatic acids are widely used in the paint and varnish industry, and that the first representatives of this class of compounds were discovered in Nature about a century ago, the synthesis of naturally occurring acids of this type has been accomplished only during recent years. And to this day triglycerides of vegetable origin serve as raw material for the manufacture of rapidly drying and durable varnishes.

This lag in synthetic work in this field is explained by the fact that the structures of most naturally occurring conjugated polyenoic acids have been established only comparatively recently. Furthermore, the presence in these compounds of a conjugated polyene system having various combinations of *cis*- and *trans*-ethylenic bonds makes them extremely unstable, with a marked tendency to undergo polymerisation, isomerisation, and oxidation. As a result, their synthesis necessitates the development of special procedures and methods, distinguished by their highly stereospecific character and the mildness of the conditions.

The methods first used to obtain these acids were based on the application of acetylenic syntheses and the Reformatskii reaction followed by dehydration and lengthening of the carbon chain. Thus stillingic acid (XLVII) and all its possible stereoisomers were synthesised in 1955 by Crombie [2] by means of the series of reactions shown in Scheme 9. Later Crombie and Jacklin used Schemes 10*a–c* to synthesise α-elaeostearic (XIX) and punicic (XXIII) acids and their stereoisomer — octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid (XLVIII) — which is not found in natural sources [4,89].

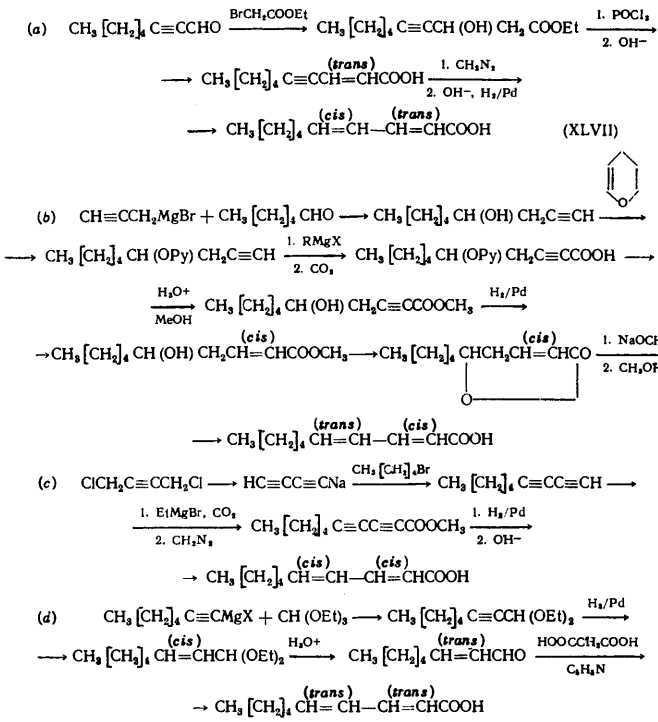
The achievement of these syntheses enabled the structures of the above naturally occurring acids to be finally established. It must be noted, however, that the above methods are characterised by many stages and low yields of the final products, while the catalytic hydrogenation of intermediate compounds containing conjugated acetylenic bonds to form *cis*-alkenes often shows little selectivity.

† *Note added in proof*. Takagi has recently obtained partial reduction products — *cis-trans*- and *trans-trans*-octadecadienoic esters — by the action of hydrazine hydrate (50° for 3 h), which causes migration of double bonds during hydrogenation, on the ethyl ester of the parinaric acid isolated from the seed oil of cultivated balsam — m.p. = 85–86° and λ_{max} = 305 nm (ε = 72400) — on the basis of which he has ascribed the *cis*-9,*trans*-11,*trans*-13,*cis*-15 configuration to parinaric acid. [136]

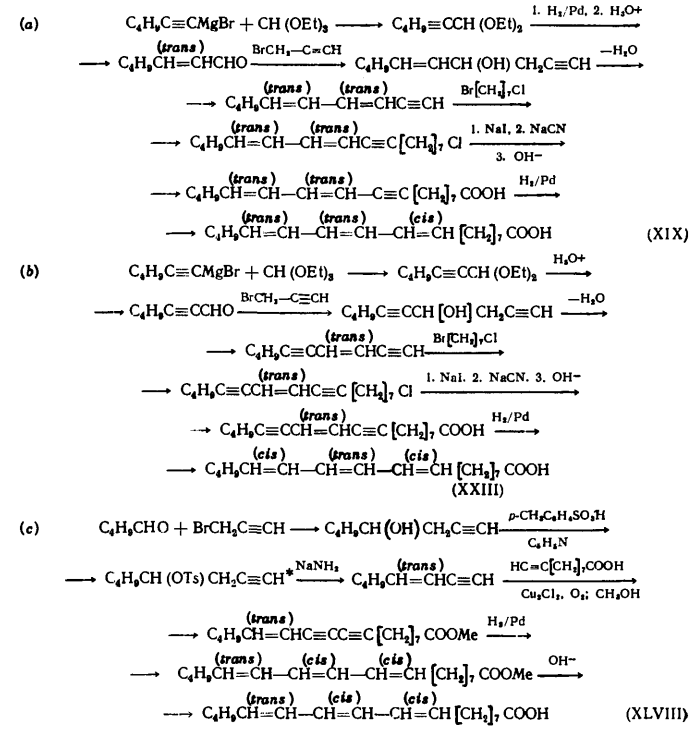
TABLE 7. Ultraviolet spectra of isomeric tetraenoic acids. [124]

Impatienic		α-Parinaric		β-Parinaric	
λ_{max}, nm	$10^{-3}\varepsilon$	λ_{max}, nm	$10^{-3}\varepsilon$	λ_{max}, nm	$10^{-3}\varepsilon$
292	45.0	292	49.5	286	59.0
305	67.7	305	72.7	299	92.8
320	58.8	320	66.3	313	87.0

Scheme 9



Scheme 10



Furthermore, these methods are of limited application, and are apparently unsuitable for the synthesis of many types of natural conjugated polyenoic aliphatic acids which have become known in recent years.

A few years ago Bergel'son et al. proposed a new method for synthesising these acids, based on the Wittig reaction, in which the general Scheme 11 was applied to the industrially available ω-chloroalkanoic acids (XLIX; R = H, X = Cl).[125-132] It was shown that the olefination of $\alpha\beta$-unsaturated aldehydes (LI) with phosphoranes (L) leads under certain conditions (in the presence of iodide ions in polar solvents) to the selective formation of a *cis*-ethylenic bond[130,131]. On the other hand, when saturated aldehydes are condensed with $\beta\gamma$-unsaturated phosphoranes (LII) in non-polar solvents, a *trans*-ethylenic bond is formed[6,132].

The application of these generalisations resulted in a new complete synthesis of α-elaeostearic acid (XIX) and of one of the isomers of calendic acid (LIII) by Scheme 12.[6,130,131] Since conjugated acids containing *cis*-ethylenic bonds are considerably more unstable than their all-*trans*-isomers, the *cis*-bond was introduced in the concluding stages. The yield of trienoic acids obtained by this method, calculated on the initial butynediol, was ~ 20%.

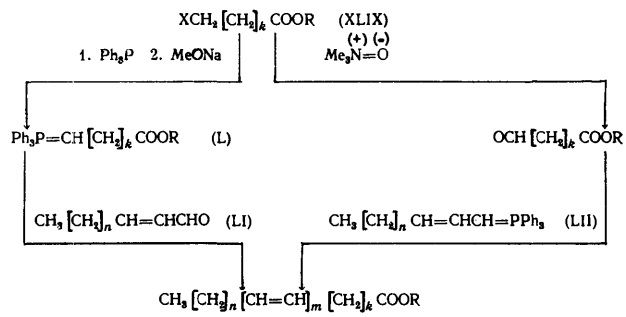
This same method was later proposed for the synthesis of octadeca-*cis*-8,*trans*-10,*trans*-12-trienoic acid (LIII) by other workers as well[133], who converted its ester, without isolating the latter, into the all-*trans*-isomer.

Two other naturally occurring conjugated trienoic acids — catalpic (XXIV) and calendic (XXVI) — were prepared for the first time by Bergel'son, Shemyakin, and their coworkers by the stereodirected *trans*-carbonyl-olefination of $\beta\gamma$-unsaturated phosphoranes according to Scheme 13.[132]

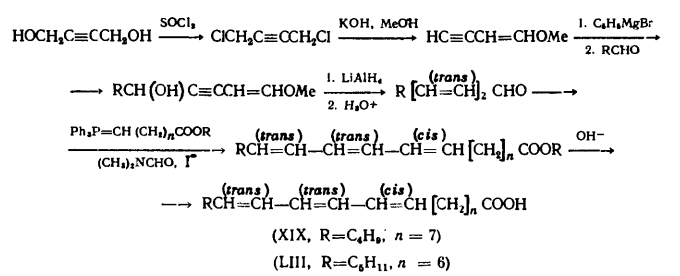
Jacarandic acid (XXXI) has been synthesised by the same investigators, using *cis*-olefination of a *cis-trans*-alkadienal in conformity with Scheme 14.[6]

* Ts = p-$CH_3C_6H_4SO_2$ (Ed. of Translation).

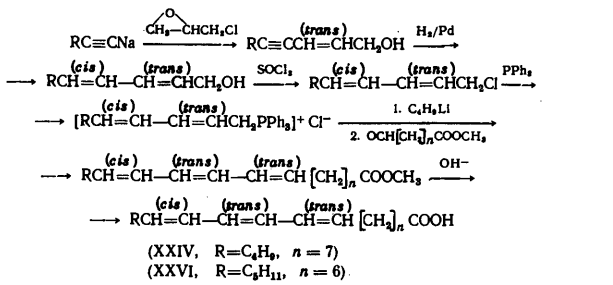
Scheme 11



Scheme 12

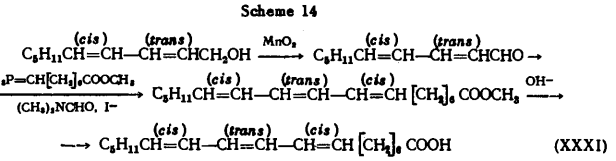


Scheme 13



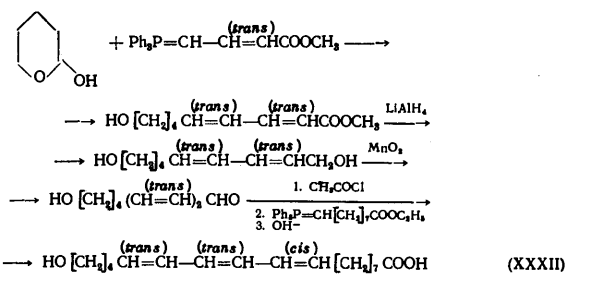
(XXIV, R=C_4H_9, $n=7$)
(XXVI, R=C_5H_{11}, $n=6$)

Scheme 14



(XXXI)

Scheme 15



(XXXII)

Bergel'son, Shemyakin, and their coworkers have synthesised the naturally occurring trienoic hydroxy-acid — kamlolenic acid (XXXII) — by successive *trans*- and *cis*--stereodirected carbonyl-olefination (Scheme 15).[134]

Dienoic and other known trienoic acids (e.g. licanic acid) can obviously be synthesised by means of stereoselective carbonyl-olefination.

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REACTIONS OF OZONE WITH ALKENES

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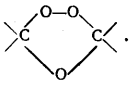
1. INTRODUCTION

Although the reaction of ozone with a carbon–carbon double bond has been known since 1855, when Schönbein was the first to accomplish the ozonisation of ethylene, a more or less clear idea of the nature of this reaction has been formulated only during the past 10–15 years. The products of ozonisation, which include, besides ozonides, α-substituted hydroperoxides, dimeric keto-peroxides, etc., occupy a prominent position in the chemistry of peroxy-compounds, owing to their ease of preparation and the possibility of converting them into aldehydes, alcohols, and other organic products. For many chemists, however, ozonisation has remained merely a means of determining the position of a double bond, and its value as a powerful synthetic tool is often underrated. The industrial application of ozonisation has recently been steadily increasing. Plant has already been operating during the past few years in which azelaic and nonanoic acids are manufactured by the ozonisation of oleic acid, and several other industrial methods have been developed[1-11]. Recent advances in the development of new applications of ozonisation and in improving the manufacture of ozone indicate that this reaction will become increasingly important in industry.

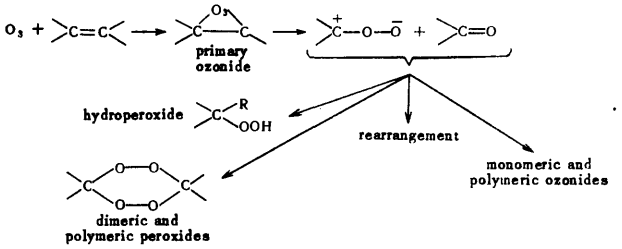
No review on ozonisation or the properties of the reaction products has been published in the Soviet literature. The foreign literature contains fundamental papers on this question[12-18], which discuss the preparation and chemical transformations undergone by ozonides of various structures. The present Reviewers have set themselves a more modest aim: this survey is concerned mainly with the synthesis of ozonides of aliphatic alkenes, a field in which research is being undertaken for the purpose of the practical exploitation of the ozonisation of alkenes for the production chiefly of higher aliphatic aldehydes, acids, and alcohols.

2. INTERACTION OF OZONE WITH ALKENES

In the early work on ozonisation, among which that of Harries[19-21] occupies an important place, many unsaturated compounds were subjected to this reaction, but no definite conclusions were reached concerning the structure of the products or the mechanism of the reaction. In 1925 Staudinger[22] suggested for an ozonide a formula comprising a five-membered peroxy–ether ring

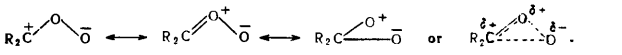


This structure was subsequently confirmed by Rieche et al.[23,24] by an alternative synthesis of the ozonide of but-2-ene. However, ozonides do not constitute the sole products of ozonisation. A more or less general mechanism of ozonisation, covering interaction with various unsaturated compounds under various reaction conditions, was suggested by Criegee and his coworkers[25-39]. This mechanism provides an explanation of most of the experimental facts known at the present time. Criegee's scheme can be represented in general as follows



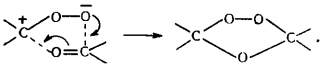
A key position in this scheme is occupied by the zwitterion, the life of which is taken to be sufficient for it to be regarded as a true intermediate product.

In most cases the primary ozonide, formed as a result of bipolar 1,3-addition of ozone to the alkene, immediately breaks down with fission of the O–O and C–C bonds by a concerted mechanism. The zwitterion is formed at one end or the other of the former double bond depending on which carbon atom receives the electron pair of the remaining C–C bond. The resulting zwitterion is stabilised by conjugation:



Stabilisation of the zwitterion can be effected in four main ways, by — (1) interaction with the simultaneously formed carbonyl compound, with formation of monomeric or polymeric ozonides, (2) dimerisation or polymerisation with formation of dimeric or polymeric peroxides respectively, (3) interaction with a proton-donating solvent with formation of hydroperoxides, or (4) rearrangement — the way in which it occurs being determined by the structure of the initial alkene, by the solvent, and to a less extent by the reaction conditions. In most cases the zwitterion reacts in more than one way simultaneously.

The first mode of stabilisation — bipolar addition of the 1,3-zwitterion to a carbonyl group[38] — usually takes place when the simultaneously formed carbonyl compound is an aldehyde:



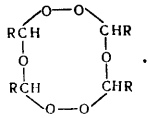
Ketones do not usually react with the zwitterion by the above 1,3-bipolar scheme leading to formation of an ozonide.

It has been noticed that most alkenes on ozonisation in an inert solvent give their "own" ozonides: i.e. a definite "cage effect" is operative. Thus the ozonisation of a mixture of oct-4-ene and hex-3-ene yields only the ozonides of

these alkenes, and the ozonisation of hept-3-ene gives only the ozonide of hept-3-ene [12]. However, this is not an absolute effect. Riezebos et al. [39] have reported the isolation of three pairs of stereoisomeric ozonides from the products of the ozonisation of methyl oleate. Loan et al. [40], while confirming the presence of a cage effect, showed, with the ozonisation of pent-2-ene as example, that some of the zwitterions jump out of the cage and enter into "extracellular" reactions even in highly dilute solution in an inert solvent. On the other hand, part of the ozonide reacts inside the cell even in the presence of excess of aldehydes, which are known to destroy the cage effect [28]. With increase in the concentration of alkene in the solvent, the relative proportions of "own" and "cross" ozonides approach the statistical values [40].

Criegee and his coworkers prepared several monomeric ozonides, purified them by distillation or recrystallisation, and determined their physicochemical constants [31]. These workers showed that only ozonides of low-molecular-weight alkenes are explosive: the ozonides of butene and higher homologues are quite stable liquids or solids, which can be subjected to distillation, crystallisation, and other operations. In all twenty-two monomeric ozonides were obtained in this work, including those of hex-1-ene, hex-2--ene, hex-3-ene, oct-3-ene, styrene, stilbene, etc. The preparation of ozonides of cyclopentene and cyclohexene had previously been reported [27]. The present Reviewers have isolated ozonides of hex-1-ene, hept-1-ene, and oct--1-ene, purified them by treatment with sodium bisulphite and fractional distillation on a column, and shown by infrared spectroscopy that the products were not contaminated with carbonyl compounds [41].

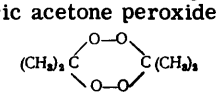
In the ozonisation of alkenes which yield monomeric ozonides as the main products, quite considerable quantities of compounds of high molecular weight are formed. Both Harries [19] and later investigators [14] have regarded these products as dimeric ozonides



Rieche et al. [24] obtained a product having this structure on synthesising the ozonide of but-2-ene from acetaldehyde and hydrogen peroxide.

The present Reviewers [42], on ozonising hex-1-ene, obtained, together with the monomeric ozonide, products of the addition to the zwitterion of two and three molecules of formaldehyde. The same work showed that a dimeric ozonide is not the main component of the residue remaining after the monomeric ozonide has been distilled off. The residue in the flask probably consists mainly of linear polymers containing a terminal hydroperoxy-group, the presence of which was confirmed by infrared spectra.

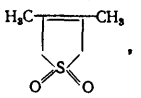
Another mode of stabilisation of the zwitterion is by its dimerisation or polymerisation. These reactions occur mainly when the carbonyl compound, formed together with the zwitterion on breakdown of the primary ozonide, is a ketone. Thus Criegee [27], on ozonising 2,3-dimethylbut-2--ene, obtained dimeric acetone peroxide



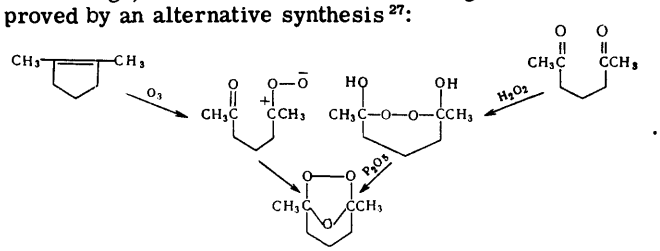
together with an extremely explosive substance, which he described as a polymer of the zwitterion $(CH_3)_2C^+-O-O^-$. Examples of other compounds which give a ketone and dimeric or polymeric peroxides on ozonisation are tetraphenylethylene [43], 1-8-octahydronaphthalene [25], bi(cyclohexylidene) [27], and bi(cyclopentylidene) [27]. Dimeric keto--peroxides can be obtained also by treating the corresponding ketones with persulphuric acid or hydrogen peroxide [16]. Polymeric peroxides have not yet been isolated as products of definite structure. They are usually described as explosive, viscous oils or amorphous solids [14,27]. Those of high molecular weight are probably linear polymers of the zwitterion $\rangle C^+-O-O^-$.

Before the publication of Criegee's work, many authors spoke of "perozonides" and "oxozonides" [12,14,20]. Most of these compounds containing more oxygen than the ozonide are probably dimeric or polymeric peroxides.

There are at least two exceptions to the rule that ozonides are not formed from compounds which give a ketone together with the zwitterion on ozonisation. The first exception is provided by cycloalkenes in which the double bond forms part of a five-membered (sometimes four--membered) ring, and the second by ketones containing an activated keto-group. Compounds of the first type include 1,2-dimethylcyclopentene [26,27,31], the cyclic sulphone [27]



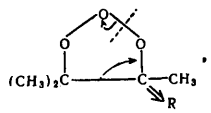
maleimide [31], certain derivatives of indene, and steroids. The ozonides of unsaturated five-membered rings are usually very stable. Thus the ozonide of the above sulphone melts at 154°, and is stable to heating (at 100° for 5 h). The driving force causing intramolecular cyclisation of zwitterions formed in the ozonisation of unsaturated rings is probably the formation of classical five- to seven-membered rings (together with five-membered trioxolan rings). Cyclohexene and cycloheptene derivatives, which would have given seven- to nine-membered rings on intramolecular cyclisation, yield mainly polymeric ozonides and peroxides on ozonisation [26,27,31]. In the case of five-membered rings, the structure of the resulting ozonides was proved by an alternative synthesis [27]:



In the ozonisation of systems containing unsaturated five-membered rings, the yield of monomeric ozonides is higher if the hydrogen atoms attached to both carbon atoms linked by the double bond have been substituted. The absence of substituents in the zwitterion and (or) the carbonyl group at the ends of the decomposition product obviously permits intermolecular reaction to compete successfully with intramolecular cyclisation. An exception is the sulphone of 5,5-dimethylhexa-1,3-diene, which gives an 85% yield of the ozonide [27]. Ozonides of this type can be obtained also by the photoactivated autoxidation of certain furans (2-methyl- and 2,5-dimethyl-furan) [44] and also dimethylisobenzofuran [45].

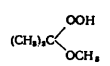
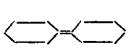
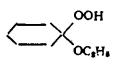
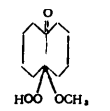
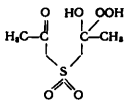
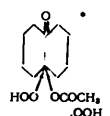
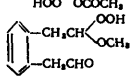
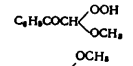
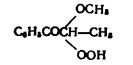
The second exception to the rule that ozonides are formed only from a zwitterion and an aldehyde is provided by the ozonisation of alkenes containing substituents possessing a considerable negative inductive effect. Criegee

et al.[34] obtained monomeric ozonides from *cis*- and *trans*-$BrCH_2C(CH_3):C(CH_3)CH_2Br$ (I), $(CH_3)_2C:C(CH_3)COOCH_3$, and $(CH_3)_2C:C(CH_3)CHO$ (II). This shows that activated ketones — bromoacetone, methyl pyruvate, and methylglyoxal — react like aldehydes with the zwitterion. Both *cis*- and *trans*-isomers of (I) give mixtures of the corresponding liquid *cis*-ozonide and solid *trans*-ozonide (dipole moments 2.45 and 2.25 D respectively). These results were obtained when (I) was ozonised in pentane, whereas when dichloromethane is used as solvent, *cis*-(I) gives bromoacetone in 90% yield together with a peroxide (presumably a dimeric peroxide of bromoacetone). The ozonide obtained by the ozonisation of (II) is the ozonide not of (II) but of 4-methylpent-3-en-2-one. The formation of the same ozonide by these two compounds is explained by the fact that the methylglyoxal obtained in the first stage reacts in both cases not at the ketonic but at the aldehyde group. The results clearly show the influence of inductive effects on the breakdown of the primary ozonide: in all cases the electron pair of the C–C bond goes to the atom having the more electronegative substituent (the alternative in which an ozonide is formed from acetone, of course, is not included):



where R = CH_2Br, $COCH_3$, CHO. However, the formation of small quantities of a mixed anhydride of formic and acetic acids, which can result only from rearrangement of the zwitterion $CH_3COCH^+OO^-$, shows that migration of the electron pair to the other carbon atom does also take place.

TABLE 1. Products of ozonisation in solvents containing an active hydrogen atom.

No.	Alkene	Solvent	Product	Yield, %	Ref.
1	$(CH_3)_2C=C(CH_3)_2$	CH_3OH		77	27
2		$CCl_4 + C_2H_5OH$		68	27
3		CH_3OH		88	25
4		acetone + water		57	27
5		acetone + CH_3COOH		—	25
6		CH_3OH		42	46
7	$C_6H_5COCH=CHCOC_6H_5$	acetone + CH_3OH		60	47
8	$C_6H_5COCH=CCOC_6H_5$ CH_3	acetone + CH_3OH		74	47

* Unstable — isolated as benzoylperoxy-derivative.

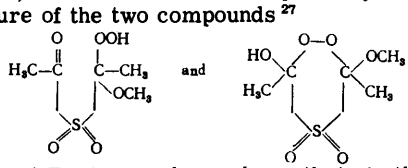
All workers regard the products obtained by the ozonisation of alkenes in solvents containing an active hydrogen atom as α-substituted hydroperoxides



where R′ is the residue of an alcohol, acid, etc. Table 1 lists several alkoxy-, hydroxy-, and acyloxy-alkyl hydroperoxides obtained by ozonolysis in "active" solvents. Many of these substances are perfectly stable, and possess high melting points (the hydroperoxide No. 4 melts at 94–95°). Hydroperoxides obtained by the ozonolysis of cyclic molecules do not preserve a simple hydroperoxide form if an aldo-group is present at the other end of the chain[48]. This is explained by interaction between the hydroperoxy- and aldo-groups with formation of peroxyhemiacetals and peroxyacetals[11].

The examples in Table 1 relate to alkenes having substituents adjacent to the double bond. Murai et al.[49] have recently subjected an unbranched-chain α-alkene, oct-1-ene, to ozonisation in ethanol. They obtained a product which, from its molecular weight and content of available oxygen, they regarded as 1-ethoxy-n-heptyl hydroperoxide.

Intramolecular reactions occur during the ozonolysis of phenanthrene[50], naphthalene[51], and indene[52] in methanol or ethanol. A tendency to cyclisation is present even when a keto-group is located at the other end of the chain. The product of the ozonolysis of the cyclic sulphone of 2,3-dimethylbuta-1,3-diene in methanol is probably an equilibrium mixture of the two compounds[27]



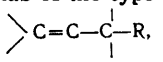
The present Reviewers have shown that, in the ozonisation of alk-1-enes in alcohols, the mode of stabilisation of the zwitterion depends on the relative proportions of alcohol and alkene. When hex-1-ene undergoes ozonisation with a hexene–ethanol molar ratio exceeding 1 : 10, formation of the hydroperoxide is accompanied by that of hex-1-ene ozonide[53].

Rearrangements, which together with epoxidation constitute a group of so-called "anomalous cases of ozonisation", are encountered far less frequently than the three types of reaction discussed above.

The ozonisation of alkenes in which groups which can cause steric hindrance are present on one of the carbon atoms joined by the double bond often results in epoxides or products of their rearrangement containing the same number of carbon atoms as the original alkene. Examples of such compounds are 1-mesityl-1-phenylethylene and 3,3,5-trimethyl-2-t-butylhex-1-ene, which on ozonisation give 2-mesityl-2-phenylvinyl alcohol[54] and an epoxide[55] respectively. Criegee[32] repeated the ozonisation of the first of these unsaturated compounds in the presence of triethylamine (to prevent rearrangement of the epoxide under the influence of the acids formed during the reaction), and obtained an epoxide which in the presence of acids readily rearranged into the enol obtained by Fuson[54]. Other cases are known of the formation of oxides of alkenes on ozonisation[56,57].

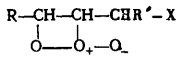
In many cases products have been isolated which contained fewer carbon atoms than would have been expected on the usual ozonolysis of the double bond. Formation of

such products has been observed most frequently in the ozonisation of compounds of the type

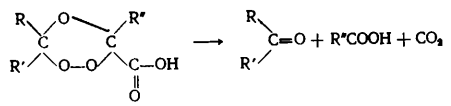


where R represents various substituents usually containing O, N, or S.

Young[58] and Leffler[62] ozonised compounds of the type RCH:CHCHR'–X (where X = Hal, OH, NR''_2, OR''', or OCOR'''') in inert solvents, and showed, from the results of a quantitative determination of the acids, that the usual products of ozonolysis are formed when X = Cl, Br, or $OCOCH_3$. They arranged the substituents X, according to their influence on the isolation of anomalous products, in the sequence Cl, Br, or $OCOCH_3 < p\text{-}OC_6H_4NO_2 < OC_6H_5 <$ $< OH < OCH_2CH_3 < N(C_2H_5)_2$. Examples of the compounds investigated by these workers are but-3-en-2-ol, which on ozonisation gives, together with formic acid (yield 75%), acetic acid (25%) (instead of lactic acid); and also CH_3CH: $:CHCH_2N(C_2H_5)_2$, giving on ozonisation, together with acetic acid (46%), formic acid (54%) (instead of diethylaminoacetic acid). The anomalous products were shown[58] to be formed neither as a result of allylic rearrangement of the initial alkene nor as a result of an oxidation process. All cases of the formation of anomalous products in large quantities involved spontaneous decomposition of peroxy-products of ozonisation with the evolution of carbon monoxide. The results were explained by rearrangement of Staudinger's "molozonide"

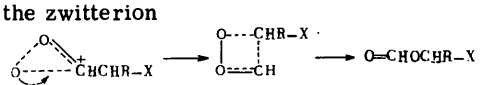


Similar results have been obtained in the ozonisation of CH_3CH:CHCOOH, CH_3CH:CHCHO, CH_3CH:$CHCOCH_2CH_3$, and several cyclic systems[59]. Barton and Seoane suggested[59] the mechanism

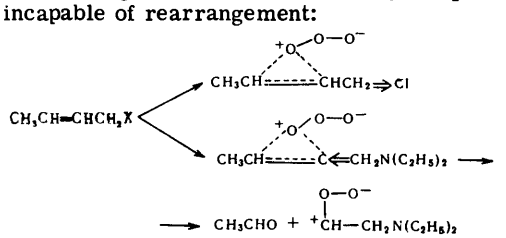


to explain the anomalous ozonolysis observed with $\alpha\beta$-unsaturated acids. This mechanism does not explain the formation of carbon monoxide.

Bailey[14] puts forward a mechanism involving rearrangement of the zwitterion



to explain anomalous ozonolysis. He interprets the increase in ability of the group X to promote rearrangement as its electronegativity diminishes in terms of the influence of inductive effects on the breakdown of the π-complex, the positive I-effect of the diethylamino-group favouring formation of a zwitterion containing X, i.e. of a zwitterion capable of rearrangement, whereas the high $-I$-effect of a halogen or $OCOCH_3$ contributes to formation of a carbonyl compound containing X and a zwitterion of type $R_2^+COO^-$, which is incapable of rearrangement:



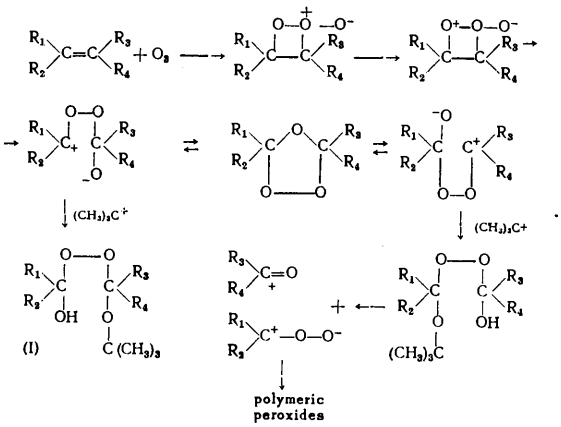
However, an anomalous course of the reaction was observed in the ozonisation of several 2-substituted naphthaquinones, which could not be explained in terms of differences between the inductive effects of the substituents[60]. Furthermore, if it is assumed that anomalous ozonolysis is caused by rearrangement at the zwitterion stage, *cis*-2--methyl-1,4-diphenylbut-2-ene-1,4-dione and 2-methylnaphthaquinone should give similar products, whereas actually the ozonolysis of these two compounds goes in opposite directions. Hence Bernatek et al.[60] have assumed that the course of anomalous ozonolysis is determined, not at the zwitterion stage, but at the stage of the primary ozonide, to which they attribute a structure in which the π-electrons are preserved (see below).

Small quantities of anomalous products are formed also in the ozonisation of "normal" alkenes. Thus the ozonolysis of dodec-6-ene yields 2–8% of valeric acid and 0.8–1.2% of butyric acid, that of cyclohexene gives 4.7% of glutaric acid and 1.8% of succinic acid[61], etc. These products are most probably formed not only as a result of rearrangement but also by the oxidation of "normal" products of ozonolysis. It is known[61,62] that the oxidation of aldehydes may yield products containing a smaller number of carbon atoms than the original aldehyde.

It is difficult to explain the formation of carbon dioxide, methane, and hydrogen in the ozonolysis of oleic acid[24], of methane from but-2-ene, of hydrogen from but-1-ene[63], and several other results.

Most anomalous products of ozonolysis are formed in inert solvents. In many cases the anomalous ozonolysis can be prevented by conducting it in methanol and then reducing the products[64]. However, the alkoxylated hydroperoxides which are formed sometimes also undergo rearrangement[30]. Anomalous ozonolysis has been observed also with the compounds C_6H_5COCR:$CHCOC_6H_5$, which give benzoic acid and methyl formate on ozonisation in methanol followed by slight heating or decomposition with alkali in the cold[47].

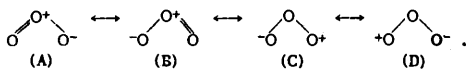
A mechanism differing somewhat from that of Criegee was suggested by Milas for the formation of peroxy-products of ozonolysis. According to this, the ozonide (the 1,2,4-trioxolan) is an intermediate in the formation of all ozonisation products. Milas postulates the existence of a zwitterion of the type $\diagdown C^+-O-O^-$, but assigns to it a subordinate role as intermediate in the formation of polymeric impurities. The main evidence of Milas' mechanism is the formation of the compound (I) on the ozonisation of alkenes in the presence of the trimethylcarbonium ion (i.e. in t-butyl alcohol and concentrated sulphuric acid)[65]:



In a later paper Milas uses the same mechanism to explain the formation of polymeric peroxides in the ozonisation of 2,3-dimethylbut-2-ene in pentane[66]. This mechanism, even if it is valid for the above cases, undoubtedly has a narrower range of application than Criegee's mechanism.

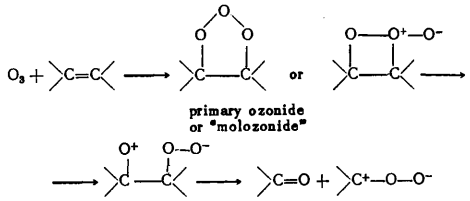
The most complex problem in the mechanism of ozonisation is the nature of the initial attack by ozone on the double bond and the structure of the primary products. This is due to the high speed of the initial reactions, which make a kinetic study extraordinarily difficult, and also the extreme instability of the initial products.

The structure of the ozone molecule is of fundamental importance to an explanation of the nature of the initial attack. Both bonds in ozone are 1.278 ± 0.002 Å long, with an angle of 116° ± 3° between them. The molecule is not paramagnetic; perhaps it is diamagnetic in the gaseous state. On the basis of these data it is represented by the following set of structures[67]



The electronic structure of the ozone molecule is such[67] that the central oxygen atom has three hybrid sp^2-orbitals lying in the same plane and one p-orbital perpendicular to this plane. Two of the three hybrid orbitals form σ-bonds with the terminal atoms, and the p-orbital forms a π-bond with one of the terminal atoms. The electrons forming this bond are delocalised. The third hybrid orbital is directed along the axis of symmetry of the molecule, and has an unshared pair of electrons. The surprisingly low dipole moment of the ozone molecule (0.56 ± 0.05 D) is explained by the fact that the high dipole moment of the third hybrid orbital operates in the opposite direction to the dipole moment of the canonical structures (A) and (B).

The addition of ozone to a double bond is usually supposed to proceed in the sequence

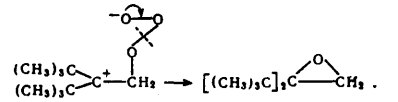


Criegee and Schröder[33] first isolated the primary ozonide of *trans*-2,2,5,5-tetramethylhex-3-ene, measured its heat of rearrangement into the usual ozonide (38.9 kcal × × mole^{-1}), and examined the reactions of this product with several substances. Reduction with sodium in liquid ammonia gave an αβ-diol. Ozonisation of the *cis*-tetramethylhexene under the same conditions did not yield a primary ozonide.

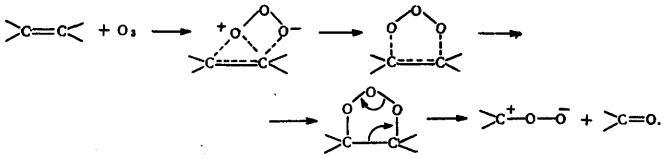
Later Schröder[68] and Greenwood[69] showed the formation of primary ozonides from *trans*-alkenes, and its absence with the *cis*-isomers, to be a general phenomenon. It was also established that the ozonisation of *cis*-2,2,5,5-tetramethylhex-3-ene yields *cis*- and *trans*-ozonides, whereas that of its *trans*-isomer gives predominantly the *trans*--ozonide[68].

Bailey et al.[70] examined the products of the ozonisation of monosubstituted derivatives of 1,4-diphenylbut-2-ene--1,4-dione with the aim of studying the mechanism of the initial attack by ozone on the double bond. The results obtained (i.e. the way in which the primary product decomposed, as a function of the substituent) pointed to none of the three schemes suggested previously — two-stage addition in conformity with the Markovnikov rule with formation of a four-membered ring (mode of decomposition determined by mesomeric effect of substituent), four-centre attack with formation of a five-membered ring (direction of decomposition determined by inductive effect of substituent), or a π-complex mechanism (the more stable of the two possible zwitterions being formed) — so that Bailey concluded that the type of attack varies with the nature of the alkene, and he listed five possible types of attack.

1. Electrophilic attack on a nucleophilic atom at the double bond, with formation of a σ-complex. This type of attack occurs, in Bailey's opinion, when marked steric hindrance is present at one end of the double bond, and it results in the formation of oxides of the alkenes:



2. Electrophilic attack on the double bond with formation of a π-complex. This type of attack takes place in the ozonisation of most unsaturated compounds†:



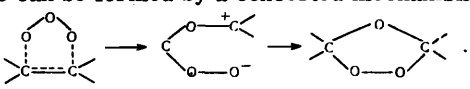
This mechanism enables most of the observed cases of ozonolysis to be explained in terms of the inductive effects of the substituents in relation to the five-membered ring of the primary ozonide. An exception is provided by *cis*- and *trans*-1,2,4-triphenylbut-2-ene-1,4-dione, whose ozonides break down in the opposite direction to that determined by the -*I*-effect of the phenyl group. In this case Bailey assumes partial maintenance of sp^2-hybridisation in the intermediate complex, and subsequent breakdown of the latter into a zwitterion by a concerted mechanism, the direction of which is determined by the mesomeric effect (+*M*) of the phenyl group.

3. Four-centre attack on the double bond with formation of a five-membered ring, which then breaks down as in mechanism 2.

4. Nucleophilic attack on an electrophilic atom.

5. Radical attack on certain saturated groupings (observed in the oxidising action of ozone).

In inert solvents and with not very stable zwitterions, an ozonide can be formed by a concerted mechanism:

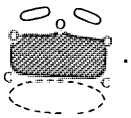


Bailey explains the formation of a primary ozonide from *trans*-2,2,5,5-tetramethylhex-3-ene, and its absence (together with a high yield of the usual ozonide) on ozonisation of the *cis*-isomer, by competition between this mechanism and the usual Criegee mechanism, such competition being governed by steric hindrance.

† In earlier papers Bailey[71] had put forward the hypothesis that the π-complex was converted into a zwitterion and a carbonyl compound without a stage involving formation of a primary ozonide.

However, the paper by Bernatek et al.[60] already mentioned gives data on the effect of the substituent in the anomalous ozonolysis of a substituted naphthaquinone which do not fit into Bailey's scheme: i.e. no correlation is observed with either the inductive or the mesomeric effects of the substituents (Table 2). From this it was concluded that the direction of ozonolysis is determined by polarisability effects at the primary ozonide stage, i.e. that the primary ozonide preserves the sp^2-hybridisation throughout its existence.

By analogy with the structure proposed by Walsh[72] for oxiran, these workers[60] assign to the primary ozonide a structure in which the p_y- and p_z-orbitals of the oxygen atoms (each containing one electron) are located in the plane of the ring, while the p_x-orbitals are perpendicular to the ring and contain two electrons. The two trigonally hybridised carbon atoms each contain one sp^2- and one p_z-orbital in the plane of the ring, together with two sp^2--orbitals above and below this plane. Overlapping between the sp^2-clouds of the carbon atoms and the p_y-clouds of the oxygen atom creates a delocalised electron cloud, which is responsible for the polarisability of the molecule. In the molecular-orbital treatment the structure of the primary ozonide has the appearance



The presence of six electrons in the delocalised orbital supports the hypothesis that the primary ozonide possesses considerable capacity for conjugation. On this hypothesis the authors derived the parameter Δ (the "absolute substituent constant"), which relates to the carbon atom of the double bond which has the largest total substituent constant:

$$\Delta_1 = |\Sigma\sigma C_1| - |\Sigma\sigma C_2| \text{ when } |\Sigma\sigma C_1| > |\Sigma\sigma C_2|$$
$$\Delta_2 = |\Sigma\sigma C_2| - |\Sigma\sigma C_1| \text{ when } |\Sigma\sigma C_2| > |\Sigma\sigma C_1|,$$

where $\Sigma\sigma C_1$ and $\Sigma\sigma C_2$ represent the sums of the substituent constants σ in the Hammett equation at one of the carbon atoms. In the case of 2-substituted naphthaquinones a satisfactory correlation was obtained between the Δi and the yield of *o*-glyoxyloylbenzoic acid.

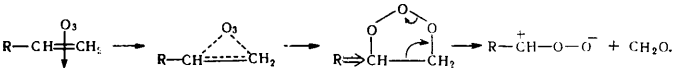
All ozonides contain a planar five-membered ring, and can therefore exist as *cis*- and *trans*-isomers. The existence of *cis*- and *trans*-ozonides was first detected by Schröder[68]. Privett and Nickell[73,74] isolated by thin-layer chromatography *cis*- and *trans*-ozonides of methyl oleate, and identified them from their infrared spectra. Riezebos et al.[39] isolated all six possible ozonides — *cis*- and *trans*-$CH_3[CH_2]_7CHO_3CH[CH_2]_7COOCH_3$, *cis*- and *trans*--$(CH_3[CH_2]_7CH)_2O_3$, and *cis*- and *trans*-$(CH_3OCO[CH_2]_7.$ $.CH)_2O_3$ — from the products of ozonisation. The products were characterised by their infrared and nuclear magnetic resonance spectra and by paper chromatography of their decomposition products (aldehydes and aldo-esters). The relative proportions of the ozonides depend on the temperature of ozonisation and the concentration of alkene in the solvent (petroleum ether). With a 10% concentration at 10° the distribution of all three above types of ozonides approximates to the statistical proportions of 2 : 1 : 1, but with a 0.5% concentration mainly the "proper" ozonide of methyl oleate is formed, the quantity of "cross" ozonides being small.

TABLE 2. Effect of substituent on yield of *o*-glyoxyloylbenzoic acid in the anomalous ozonolysis of 2-substituted 1,4-naphthaquinones.

Substituent	Yield, %	Substituent	Yield, %
—OH	90.4	—NHCOCH$_3$	13.8
—Cl	78.4	—O$^-$(OH + pyridine)	9.7
—C$_6$H$_5$	71.8	—NH$_2$	4.6
—OCOCH$_3$	71.3	—OCH$_3$	3.9
—N(CH$_3$)$_2$	21.0		

The formation of "cross" ozonides in the ozonolysis of methyl oleate brings us back to the question of the role of the "cage" of solvent molecules in the interaction of the zwitterion with the aldehyde. Escape of the zwitterion from the "cage" is fairly widespread in ozonisation. Loan et al.[40] ozonised pent-2-ene in the absence of solvent at -70°, and obtained a mixture of the ozonides of pent-2-ene, but-2-ene, and hex-3-ene in proportions close to random (2 : 1 : 1). When the initial ozonide was diluted with pentane, the yields of "cross" ozonides diminished. These workers observed that reaction takes place in the "cage" even in the presence of excess of a "foreign" aldehyde. From the relative proportions of the ozonides formed in this case it was assumed that 9.5% of the product recombines in the "cage", 51% yields the free zwitterion $CH_3CH^+OO^-$, and 39.5% gives the free zwitterion $CH_3CH_2CH^+OO^-$.

The experimental facts reported above and their interpretation permits us to make the following hypotheses concerning the course of the ozonisation of alk-1-enes of normal structure. On the basis of a scheme involving a π-complex passing into a molozonide five-membered ring, which is applicable to most alkenes, the direction of breakdown of the primary ozonide should be determined by the inductive effects of the substituents adjacent to the double bond. Since the distribution of inductive effects in this case is obvious — zero effect of hydrogen atoms and a positive inductive effect of an alkyl substituent — ozonisation of an alk-1-ene should involve formation mainly of an alkyl-substituted zwitterion and formaldehyde:



When the reaction is conducted in an inert solvent, the zwitterion reacts with the formaldehyde — the most reactive of the unsubstituted aldehydes — to form a monomeric ozonide. Some of the zwitterions may escape from the cage, but in view of the preferential occurrence of breakdown by the above mechanism, opportunities for the formation of "cross" ozonides are very limited. Ozonisation in active solvents — alcohols, carboxylic acids, etc. — should yield mainly the corresponding derivatives of the zwitterion $\diagdown CH^+OO^-$ and formaldehyde.

3. PROPERTIES OF OZONISATION PRODUCTS

It follows from the discussion in Section 2 that the main products of ozonisation are monomeric and polymeric ozonides, dimeric and polymeric peroxides, and also products of ozonisation — α-substituted hydroperoxides — in active solvents. Very little is known about the chemical properties of the ozonisation products. Ozonides have been somewhat more fully studied, but of dimeric and polymeric peroxides it is known only that in most cases they are explosive, viscous oils. Almost nothing is known also of the structure of the polymeric ozonides.

Since the first application of ozonisation was to determine the position of the double bond in unsaturated compounds, investigation of the products of ozonisation began with a study of methods for their conversion into stable products — acids, aldehydes, alcohols, etc. — which could be identified. For the most part these methods consisted merely in oxidation, reduction, thermal decomposition, and hydrolysis. Many of them were at one time patented, but only a few of them found industrial application.

Ozonolysis followed by oxidation is most often employed as a method for determining the position of a double bond. Asinger's method[75] — ozonisation in a hot suspension of silver oxide in the solvent — is generally used. It converts alkenes quantitatively into acids. Asinger has recently supplemented this method with gas-chromatographic analysis of the acids as their methyl esters[76]. Very often the decomposition products are oxidised with oxygen, while ozone or a metal salt is used as initiator. The firm Emery Industries Inc. uses this method to produce azelaic and nonanoic acids on an industrial scale from oleic acid of vegetable origin[1]. The very promising method of Otsuki and Funahashi[77] consists in ozonising oleonitrile and then subjecting the product to oxidising decomposition with formation of the 8-cyano-octanoic acid, which was then reduced to 9-aminononanoic acid. Examples of the oxidative ozonolysis of other compounds are given in Table 3. Several patents have been taken out on oxidative ozonisation[7-9]. Besides the oxidising agents which have been listed, use is made also of hydrogen peroxide as an aqueous solution or mixed with acetic, sulphuric, or formic acid. These methods have been described in the reviews by Long[12] and by Bailey[14]. Oxidative decomposition is sometimes accompanied by rearrangements[61].

Reduction of the ozonisation products is, perhaps, the method showing the greatest industrial promise. Existing methods of reduction can be divided into two groups — reduction to aldehydes and ketones, and reduction to alcohols.

For preparative purposes use is made most often of reduction with sodium or potassium iodide, reduction with zinc or magnesium in the presence of water or acetic acid[12,14], and also catalytic reduction on palladium or other catalyst[28,78,79]. Other reducing agents are sodium bisulphite, sulphur dioxide, tin(II) chloride, and formaldehyde. Examples of these reactions are given in Table 4.

Reduction of the ozonides with hydrogen on a Lindlar catalyst[79] at 0°, followed by gas-chromatographic analysis of the resulting aldehydes, is sometimes used for determining the position of a double bond.

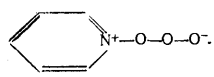
TABLE 3. Oxidative decomposition of products of ozonolysis.

Compound ozonised	Solvent	Product (acid)	Method of decomposition	Yield, %	Ref.
Cyclohexene	CH_3OH	adipic	$O_2 - O_3$, HCOOH	73	80
»	»	»	ditto	85	48
»	CH_3COOH	»	CH_3COOH	86	81
Oct-1-ene	CH_2Cl_2	heptanoic	$O_2 - O_3$, CH_3COOH	83	13
Dodec-1-ene	CH_3COOH	undecanoic	$O_2 - O_3$, CH_3COOH	77	13
»	pentane	»	Ag_2O + NaOH	93	75
Tridec-1-ene	$CHCl_3$	lauric	ditto	94	75
Naphthalene	CH_3OH	phthalic	$O_2 - O_3$, HCOOH	88	51
cis-Octadec-9-enylamine	CH_2Cl_2	9-aminononanoic	air, Mn catalyst, HCl	25	77

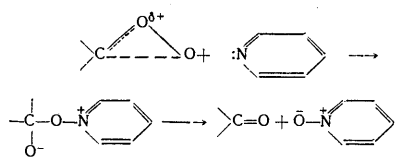
TABLE 4. Reduction of ozonisation products.

Compound ozonised	Product	Solvent	Method of reduction	Yield, %	Ref.
Cyclohexene	adipaldehyde	CH_3OH	catalytic	54	79
1,2-Dimethyl-cyclopentene	heptane-2,6-dione	CCl_4	»	74	31
Stilbene	benzaldehyde	$CH_3OH + CH_2Cl_2$	steam	93	13
Styrene	»	ditto	»	37	13
Phenanthrene	biphenyl-2,2′-dial	CH_3OH	NaI	84	82
Camphene	camphenilone	CH_3OH	NaI	75	30

The reduction of ozonisation products to aldehydes and ketones is used in the preparation of piperonal from isosafrole and of vanillin from isoeugenol[83]. The reducing agents tried in this work were $NaHSO_3$, $FeSO_4$, $K_4[Fe(CN)_6]$, $SnCl_2$ + HCl, Sn + HCl, Zn + CH_3COOH, $(NH_4)_2Fe(SO_4)_2$, KI + CH_3COOH, H_2O + Zn, $AgNO_3$, quinol, pyridine, and piperidine. An aldehyde (3-oxobisnorchol-4-en-22-al) is formed also in the ozonolysis of ergosta-4,22-dien-3-one[84]. The role of added pyridine in these reactions is very interesting. Pyridine considerably increases the yield of piperonal and of the above hormone. The direction of the reaction on ozonisation in pyridine medium is probably a result of complex formation between pyridine or pyridine oxide (formed on ozonisation) and ozone[85]. This diminishes the electrophilic character of the ozone molecule, which can then react only with the most electron-donor double bond:



In the presence of pyridine the above steroid, as well as isosafrole, yields two moles of aldehyde, whereas in the absence of pyridine only one mole of aldehyde is formed. This is probably explained by the pyridine attacking the zwitterion with formation of pyridine oxide and the aldehyde:



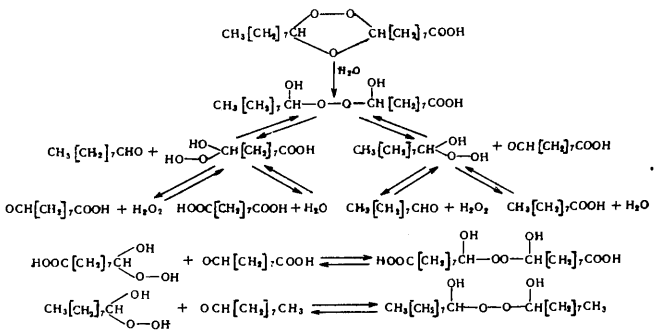
Catalytic reduction has been used for the production of 9-aminononanoic acid. In one case the products of the ozonolysis of oleic acid were reduced in two stages, the second stage of reduction being conducted in the presence of ammonia or hydroxylamine[10,86]. Recently Pollart and Miller[87] have proposed a single-stage method of reduction without preliminary isolation of the carbonyl compounds. Hexamethylenediamine has been obtained similarly by the ozonolysis of cyclohexene. 9-Aminononanoic acid and hexamethylenediamine are starting materials for the manufacture of 9-nylon and 6,6-nylon respectively.

Treatment of the products of ozonisation with an acid solution of 2,4-dinitrophenylhydrazine yields hydrazones of the aldehydes[88].

Lithium tetrahydroaluminate, sodium tetrahydroborate, Grignard reagents, and methyl-lithium have been used to reduce the peroxy-products of ozonolysis to alcohols. Greenwood[89] reduced the ozonisation products of oct-1-ene, oct-3-ene, and hept-2-ene in hexane with lithium tetrahydroaluminate, and obtained respectively heptan-1-ol (95%), propan-1-ol + pentan-1-ol (87%), and pentan-1-ol (89%).

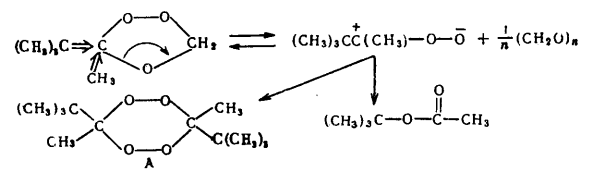
Criegee and Schröder[33] reduced the product of the ozonisation of *trans*-2,2,5,5-tetramethylhex-3-ene at -80° to -100°, which they termed the primary ozonide, with lithium tetrahydroborate, sodium tetrahydroborate, hydrogen iodide in ether, sodium in liquid ammonia, hydrogen on Raney nickel, methylmagnesium bromide, and isopropylmagnesium bromide. Besides the carbinol (neopentanol) found in all cases (other than hydrogen iodide and hydrogen), reduction with sodium in liquid ammonia gave a considerable quantity of a diol (2,2,5,5-tetramethylhexane-3,4-diol). Greenwood[90] obtained α-diols by reducing the ozonides of several other *trans*-alkenes (hex-3-ene, etc.). Sparks and Knobloch[91] reduced the products of the ozonisation of alk-1-enes with a Grignard reagent, and obtained in all cases the corresponding carbinols (products of the addition of the Grignard reagent). In later work Greenwood and Haske[69,92] have shown that, when the ozonide of hex-3-ene is reduced with isopropylmagnesium bromide, the main product is that resulting from addition of the Grignard reagent to propionaldehyde — 2-methylpentan-3-ol — accompanied by propane and propene.

Very little work has been done on the hydrolysis of ozonisation products. In most cases simultaneous formation of aldehydes and acids has been noted. The only mechanism of hydrolysis which has been suggested, in connection with an investigation by Rieche et al.[24] on the ozonide of oleic acid, involves as the first stage cleavage of the ether bridge in the ozonide molecule with formation of a peroxy-diol:

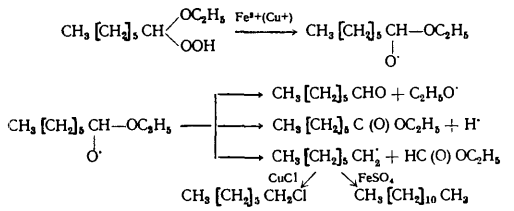


Evidence for this mechanism is the isolation, from the mixture resulting from hydrolysis of the ozonide, of products which the authors identified as 1,1′-peroxydinonanol and 9,9′-dihydroxy-9,9′-peroxydinonanoic acid. In a later paper[15] Rieche put forward the hypothesis that hydrolysis of an ozonide, like its formation, involves an intermediate stage in which a zwitterion is formed.

Very little work has been done also on the thermal decomposition of peroxy-products of ozonisation. Heating the ozonisation products of most alkenes usually gives complicated mixtures of unidentifiable products. Exceptions are the decomposition of naphthalene ozonide, which gives an 87% yield of phthalaldehydic acid when heated in methanol[51], and also the formation of a 69% yield of 2′-formylbiphenyl-2-carboxylic acid when the ozonide of phenanthrene is heated in methanol[50]. Sometimes rearrangements are observed on thermal decomposition. Criegee et al.[31] decomposed the ozonide of 2,3,3-trimethylbut-1-ene and obtained polymers of formaldehyde, a dimeric peroxide (A), and t-butyl acetate. They assumed that the latter two products were formed from a zwitterion containing a t-butyl radical:

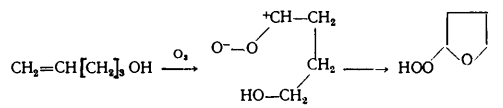


Murai and Sonoda[49] have investigated the reaction of the ozonisation products of alkenes in alcohols. They reduced the product of the ozonisation of oct-1-ene in ethanol (which they termed 1-ethoxy-n-heptyl hydroperoxide) with aqueous solutions of iron(II) sulphate and of copper chlorides, and obtained ethyl formate, heptanol, ethyl heptenoate, hexyl chloride (in the case of cuprous chloride), and dodecane (with ferrous sulphate). Homolytic breakdown of the hydroperoxide was suggested as the reaction mechanism:

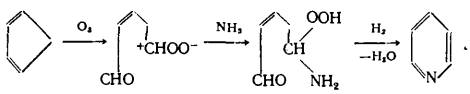


Diaper and Mitchell[93] ozonised ethyl undec-10-enoate in ethanol, subjected the product to alcoholysis at 28–170°, and obtained diethyl sebacate as the main product. They showed that the ester was formed mainly as a result of rearrangement of an alkoxy-hydroperoxide.

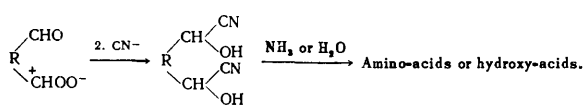
Several interesting reactions occur in the ozonisation of alkenes containing other functional groups, and also when ozonisation takes place in the presence of other compounds. Thus the ozonisation of unsaturated alcohols has been observed to involve cyclisation by the mechanism[94]



A very interesting type of ozonisation has been described by Fremery and Fields[95]. When cyclopentadiene is ozonised in the presence of ammonia or an amine, a hydroperoxide is formed which on reduction and dehydration yields pyridine:



The ozonisation of cycloalkenes in the presence of hydrogen cyanide results in the formation of biscyanohydrins, which can then be converted into amino-acids and hydroxy-acids[96]:



The number of technical processes based on ozonisation is at present limited, and production by these methods is on a small scale. However, the situation in this field should change in the immediate future. This is because of the great amount of research being undertaken and by

the rapid development of the technique of ozonisation. With respect to cost as an oxidant, ozone now occupies the second place after oxygen, which enters the final oxidation product‡.

Work undertaken at the Institute for Organic Chemistry of the German Academy of Sciences in Berlin is of great interest. Bertsch and his coworkers[97] have investigated the ozonisation of alk-1-enes with dodec-1-ene as example at temperatures between -20° and +20°. From the results obtained these workers carried out the ozonisation of the Kogasin fractions of the products of the Fischer–Tropsch synthesis (the 200–210°, 210–220°, and 220–235° fractions containing respectively 41%, 36%, and 32% of alkenes, mainly alk-1-enes), followed by decomposition of the ozonides with water vapour and hydrogenation over Raney nickel at 1–2 atma and 20°. Under these conditions aldehydes were reduced to alcohols, while acids remained unchanged. The yields of products obtained from the fractions were 16–19% of acids, 14–18% of alcohols, and 1.5–2.0% of aldehydes.

Thus the alkenes present in the Kogasins have been completely converted into oxygen-containing products. In later work Greiner and Wagner have studied the kinetics of the addition of ozone to alkenes in the liquid phase[98], the way in which formaldehyde is produced in the ozonisation of alkenes containing terminal and non-terminal double bonds[99], the rates of ozonisation of various alkenes[100], the design of ozonisers[101], and methods for the conversion of ozonisation products into acids[102,103].

Among other methods which have found technical application, mention must be made of the synthesis of strychnine[104] and certain hormones[84], and also the syntheses of piperonal from isosafrole and of vanillin from isoeugenol. Indo[83] made a detailed study of the latter two syntheses, established the structure of the intermediate peroxy-compounds, and worked out several reduction methods aimed at obtaining the maximum yields of vanillin and piperonal.

4. METHODS OF ANALYSIS OF PEROXY-PRODUCTS OF OZONISATION

Although the decomposition products of ozonides and peroxides can be determined by widely used and well studied methods, considerable difficulties are involved in analysing the peroxy-products themselves. In isolated cases use can be made of elementary analysis, determination of available oxygen, measurement of molecular weight, etc., the possibility of using a particular method being governed by the properties of the product to be analysed. In the elementary analysis, ozonides of alk-1-enes (from C_4 upwards) burn quite quietly (if the sample does not exceed 5 mg), but do not liberate iodine quantitatively on reaction with potassium iodide; polymeric products of ozonisation deflagrate when an attempt is made at elementary analysis. Molecular weights are best determined cryoscopically in benzene or bromoform, dichloroethane, etc.[105] Rast's method is unreliable, since the substances under investigation often decompose at the temperatures at which determinations are made by this method.

Peroxy-products of ozonolysis can be arranged in the sequence — hydroperoxides > ozonides > dimeric peroxides — according to ease of interaction with iodides. The reaction is quantitative only with hydroperoxides or ozonides which yield ketones on reduction. Ozonides and peroxides which give aldehydes on reduction often undergo rearrangement into carboxylic acids, which results in a diminution in the quantity of iodide oxidised. Dimeric peroxides often react very slowly.

The infrared spectra of ozonides have been investigated in some detail. Briner and his coworkers at first wrongly assigned to ozonides absorption bands in the region of the carbonyl group[106]. It was subsequently shown that these bands were due to contamination with carbonyl compounds formed by decomposition of the peroxy-products[28,41]. Criegee et al.[31] reported that thirteen out of eighteen ozonides contained an absorption band in the range 9.4–9.6 μm in the infrared spectrum, while the remaining ozonides absorbed at 8.8–9.4 or 9.6–10.0 μm. The present Reviewers have detected[41] two absorption bands — at 1110 and 1062 cm^{-1} — with all products of the ozonisation of n-alk-1-enes, and have regarded them as characteristic of the C–O bonds in an ozonide. Riezebos et al.[39] have observed absorption bands at 1110 cm^{-1} with the six isomeric ozonides of methyl oleate, together with bands at 830 and 1320 cm^{-1} with the *cis*- and *trans*-isomers respectively. Privett and Nickell[74] have also reported the same bands in the spectra of the *cis*- and *trans*-ozonides of methyl oleate. Similar differences have been found by Schröder[68] in the spectra of the stereoisomeric 2,2,5,5-tetramethylhex-3--enes. Greenwood and Haske[69,92] have compared the infrared spectra of hex-3-ene ozonide and di-n-propyl peroxide and have found several coincident bands — at 950, 1380, and 1460 cm^{-1} compared with 955, 1375, and 1453 cm^{-1} — for the two compounds. Loan et al.[40] have observed strong absorption at 1080–1110 cm^{-1} in the infrared spectrum of the ozonide of but-2-ene, which they have attributed to the ozonide group.

Calculations based on the tetra-atomic model molecule C–O–O–H have shown[107,108] that the infrared spectrum of a hydroperoxide should contain the bands listed in Table 5. From a study of the infrared spectra of several hydroperoxides and peroxyalkanols in the region of the hydroxyl--stretching vibrations[108] Terent'ev and his coworkers have assigned to vibrations of a free (or an intramolecularly hydrogen-bonded) hydroxyl the values 3580–3560 cm^{-1} for hydroxyl attached to a carbon atom combined with a peroxy-group, and ~3530 cm^{-1} for a hydroperoxy-hydroxyl.

The nuclear magnetic resonance (n.m.r.) spectra have also been studied with many ozonides. The signals obtained in the n.m.r. spectrum at 30 Mc/s with methyl oleate[39] are listed in Table 6.

TABLE 5. Absorption bands (cm^{-1}) in the infrared spectra of hydroperoxides.

Structure	Calc. for COOH	Cumene hydroperoxide	
		calc.	found
C—O—O	586	597	585
CO—OH	834	838	840
O—O	886	888	886
C—O	1156	1285	1270
O—O—H	1321	1324	1325
O—H	3450	3450	3556

‡ The price of ozone per kilogramme is 17 cents in the USA and from 25 pfennigs in Western Germany.

TABLE 6. Signals due to products of the ozonisation of methyl oleate in the n.m.r. spectrum.

Ozonide	1.1 ppm	1.4 ppm	2.3 ppm	3.7 ppm	5.1 ppm
$(CH_3[CH_2]_7CH)_2O_3$	+	+	–	–	+
$CH_3[CH_2]_7CHO_3CH[CH_2]_7COOCH_3$	+	+	+	+	+
$(CH_3OCO[CH_2]_7CH)_2O_3$	–	+	+	+	+

Note. 1.1 – CH_3; 1.4 – CH_2; 2.3 – CH_2COOCH_3; 3.7 – O–CH_3; 5.1 – $CH\langle^{O-O}_{O}\rangle CH$–.

The n.m.r. spectrum of the ozonide of hex-3-ene contained[69] two overlapping triplets with centres at 4.90 and 4.94 ppm, a multiplet at 1.55 ppm, and two very close and overlapping triplets at 0.8 ppm. These signals were attributed respectively to methine, methylene, and methyl protons of the ozonide.

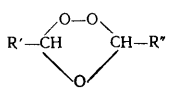
Loan et al.[40] observed in the n.m.r. spectrum of the ozonide of but-2-ene a doublet at 8.65 ppm (CH_3) and two overlapping quartets at 4.72 and 4.78 ppm (*cis*- and *trans*--CH). The n.m.r. spectrum of the ozonide of pent-2-ene showed a multiplet at 5.13 ppm (CH), a multiplet at 8.37 ppm (CH_2), a doublet at 8.65 ppm ($CH–CH_3$), and a triplet at 9.04 ppm ($CH_2–CH_3$). Finally, two overlapping triplets at 4.95 ppm (CH), a multiplet at 8.34 ppm (CH_2), and a triplet at 8.61 ppm (CH_3) were found in the n.m.r. spectrum of the ozonide of hex-3-ene.

Gas–liquid chromatography has also been used for the analysis of ozonides. Schröder[68] has employed a GESF--96 column to separate the *cis*- and *trans*-ozonides of hex--3-ene. Greenwood and Haske[69,92] used a cyanosilicone and diethylene glycol succinate for the same separation.

Thin-layer chromatography is often used for the analysis of ozonides and other peroxy-products of ozonisation, and for their isolation during preparation. A large number of solvents and reagents have been described which can be used for the separation and identification of various peroxides[109,110]. The analysis and identification of the peroxy-products of ozonolysis still remains in general a very difficult task, requiring the combined application of several methods of analysis.

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As long ago as the first decade of this century chemists who had studied the reaction of ozonisation were concerned with the possibility of its wide practical application. The hydrolysis of unsymmetrical ozonides



yields as final products mainly the aldehydes R'CHO and R"CHO and the acids R'COOH and R"COOH. The mixtures of valuable oxygen-containing products obtained by the ozonisation of individual alkenes can be separated comparatively easily.

The ozonisation of alkenes is a rapid process, and the alkenes react completely. However, the explosive properties of many ozonides, and especially of the highly polymeric products obtained on the ozonolysis of alkenes, for many years halted work aimed at the wide practical application of this interesting reaction. Most researches were directed at the use of ozonolysis for studying the structure of organic compounds containing unsaturated bonds.

During this time vast experience has been ascumulated, and a detailed study has been made of the mechanism of the reaction and the chemistry of processes involved in the ozonisation of alkenes and the decomposition of ozonides. The technique of ozonisation has been brought to such a degree of perfection that this reaction can be accomplished to a large extent without danger, so that ozonisation of the higher alkenes can be applied on an industrial scale. An especially important future awaits the processing of higher alk-1-enes into oxygen-containing products – higher aliphatic acids, aldehydes, and alcohols.

The higher C_{7-18} alk-1-enes can be obtained relatively easily by the cracking or the high-speed cracking of alkanes. The resulting products can be separated without special difficulty into individual alk-1-enes from C_7 to C_{16}, which permits the production on their basis, by the application of ozonisation, of several individual oxygen-containing products of immense value to the national economy of the Soviet Union.

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STABILISATION OF CONCENTRATED OZONE

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The chemical properties of ozone are characterised by two essential features: its chemical instability and its powerful oxidising action. At low concentrations (and in the absence of impurities) ozone decomposes quite slowly under normal conditions. At high concentrations ozone decomposes explosively. Ozone also behaves as a priming explosive in the liquid state (b.p. -111.9°) and in the solid state (m.p. -192.7°).

The applications of ozone in many areas of science and technology are becoming progressively wider: many workers have sought to prepare pure concentrated ozone and have investigated inert solvents which enable the gas to be separated from oxygen and stabilised.

Ozone is prepared, in the form of ozone–oxygen mixtures containing about 8–9 wt.% of ozone, by subjecting oxygen to the action of a silent discharge in ozonisers. The ozone may be concentrated by liquefaction, for example, in the apparatus shown in Fig. 1. Since the explosive propensities of ozone are largely determined by impurities, particularly those of organic origin, the oxygen fed to the ozoniser must be thoroughly purified. Methods of purification have been described in detail in papers [1,2] and also in a patent specification [3]. According to Platz and Hersh [1], if the concentration of organic compounds (expressed as CO_2) in the oxygen is less than 20 parts per million, it is possible to prepare stable 100% liquid ozone by liquefaction. Liquid ozone–oxygen mixtures also can be prepared by liquefaction — for example, by using the apparatus shown in Fig. 2 — because above -180° liquid ozone is miscible in all proportions with liquid oxygen. This is clear from the ozone–oxygen phase diagram [4] given in Fig. 3.

However, the explosion hazards of concentrated ozone depend not only on the presence of impurities, but also on local shock; hence the current interest in the use of inert sorbents or solvents to allow safe storage, transfer, and manipulation of concentrated ozone.

Studies of the adsorption isotherms of ozone on silica gel over a range of temperatures [5,6] have shown that the sensitivity of adsorbed ozone as an explosive is low. This allows ozone to be desorbed almost quantitatively by slightly raising the temperature (say, from -150° to -120°), thus providing a ready means for evolving concentrated ozone from the gas phase by an adsorption–desorption cycle.

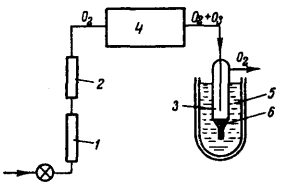


Fig. 1. Liquefaction of ozone:
1) column for oxygen purification; 2) flowmeter; 3) trap; 4) ozoniser; 5) refrigerant; 6) condensed ozone.

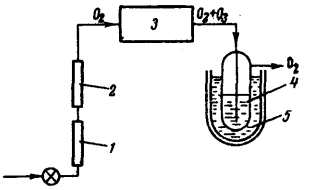


Fig. 2. Liquefaction of ozone–oxygen mixtures:
1) column for oxygen purification; 2) flowmeter; 3) ozoniser; 4) trap; 5) refrigerant.

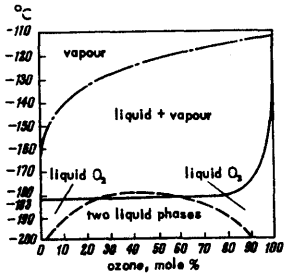


Fig. 3. Phase diagram for the ozone–oxygen system.

Up to 1960, carbon tetrachloride was the only solvent known to be inert towards ozone. However, this solvent has a very low solubility coefficient [7] (4.6 at -12°), and a relatively high melting point (-22.96°). Furthermore, there is a possibility of traces of phosgene being formed after prolonged contact between carbon tetrachloride and ozone. Nevertheless, it has been suggested [8] that liquid ozone can be stabilised by the addition of 0.5–25% of carbon tetrachloride.

A search for a new solvent, made by a group of French workers [9-16], led to the Freons, whose solubility coefficient for ozone at -110° is of the order of 1500–3500. The Freons are inert towards ozone because of the stability of the C–F bond (the bond energy for this class of compounds varies between 90 and 112 kcal mole^{-1}). The presence of traces of free fluorine in Freons has a stabilising effect on ozone. Ozone dissolved in Freons retains its chemical identity, and does not form complexes or solvates. Freons have a low solidification temperature, which assists the dissolution of ozone. Because of the chemical inertness of Freons, apparatus for working with these compounds can be constructed from a wide range of materials.

Ozone can be separated from oxygen at the ozoniser outlet by dissolution in a Freon, whereas oxygen does not dissolve. The solubility of ozone in Freons depends on the nature of the Freon, and is limited by the solidification temperature of the latter. The melting points and boiling points of the Freons used for dissolving ozone are set out in the first two lines of Table 1.

TABLE 1. Solubility coefficients for 100% ozone in various fluorochloromethanes and fluorochloroethanes.

Freon	CF-11	CF-12	CF-13	CF-22	CF-113	CF-114	CF-14
Formula	CCl_3F	CCl_2F_2	$CClF_3$	$CHClF_2$	$C_2Cl_3F_3$	$C_2Cl_2F_4$	CF_4
M.p., °C	−111	−158	−181	−160	−35	−94	−183.8
B.p., °C	+23.8	−29.8	−81.4	−40.8	+47.6	+3.5	−128.8
Temperature, °C	Solubility coefficient S_B^T (pressure dependent)						
−110±1	8.3—9	12—14	13—15	21—22			
−94±1	4.1—4.4	4.4—4.5					
−63±1	1.2—1.3					1.2—1.4	
−23±1	0.3—0.35				0.485—0.495		
	Solubility coefficient S_B^T (100%)						
−110±1	1610±80	2090±80	2180±80	3490±80			
−94±1	132±5	136±5				35±1	
−63±1	25.4±0.2				9.4±0.2		
−23±1	6.6±0.3						

The best solvent and stabiliser for liquid ozone is Freon-14. The phase diagram[17] for the liquid ozone–liquid Freon-14 system is reproduced in Fig. 4.

Two types of apparatus are used to dissolve ozone in Freons, depending on whether the melting point of the Freon is higher or lower than the boiling point of ozone (-111.9°). In the former case dissolution is obtained by bubbling the gas through liquified Freon to saturation. In the latter case the ozone and Freon are liquified simultaneously in a small distillation column to which the two gases are admitted in countercurrent. Fig. 5 shows the general layout of the apparatus; Fig. 6 is a more detailed sketch of the cell used for dissolution. The Freons are previously purified (to the 99.99% level) by distillation followed by drying with activated gels, 5 A zeolite, and phosphorus pentoxide. They are then condensed in a graduated vessel which has been carefully dried. A predetermined volume of Freon is distilled into the ozone saturator cell, also carefully dried. The saturation time depends on the temperature, pressure, and nature of the Freon. The saturation limit for a number of Freons was reached at -110°. The longest duration of the experiments was 6 h. When calculating the solubility, allowance was made for the "dead volume" of the cell (the space above the liquid phase) and for the mass of solvent lost by evaporation whilst bubbling the ozone–oxygen mixture. The solubility data, expressed as the Bunsen coefficient

$$S_B^T = \frac{V_{O_3}}{V_F}\frac{760}{P},$$

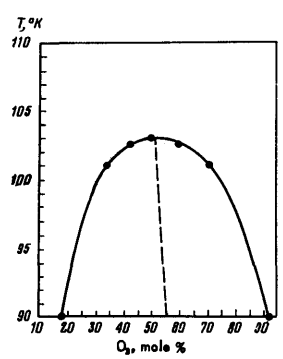


Fig. 4. Phase diagram for the liquid ozone–liquid Freon-14 system.

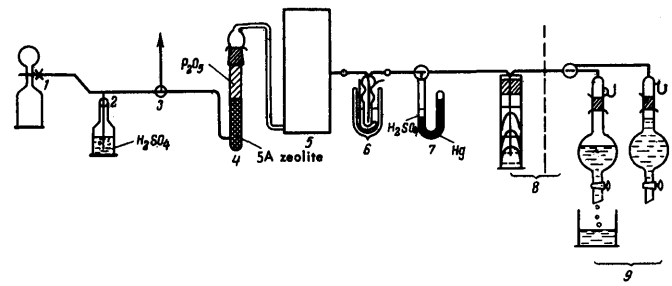


Fig. 5. Apparatus for dissolving ozone in Freons: 1) oxygen cylinder; 2) manostat; 3) oxygen discharge; 4) drying tube; 5) ozoniser; 6) dissolution cell; 7) manometer; 8) absorption towers; 9) volume meters.

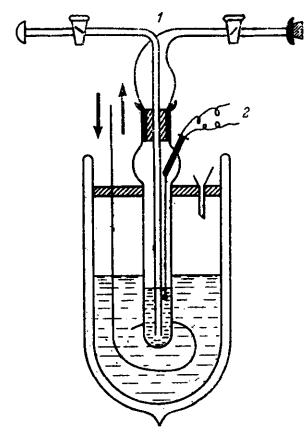


Fig. 6. Cell for ozone dissolution: 1) ozone inlet tube; 2) thermocouple.

where V_{O_3} is the volume of dissolved ozone under normal conditions, V_F is the volume of Freon at temperature T, and P is the effective total pressure in mmHg, are tabulated in lines 3–6 of Table 1. The remaining lines of the table list the solubility data expressed as the Bunsen coefficient, $S_B^T(100\%)$, for one atmosphere.

The best solvent for gaseous ozone is Freon-22, monochlorodifluoromethane $CHClF_2$, because it has a low molar volume.

Some mixtures of the Freons, for example a 50% mixture of CF-114 and CF-11, offer a higher solubility than the pure components. An increase in solubility with decrease in molar volume is observed on going from Freon-11 to Freon-12 and -13, in which ozone exhibits virtually ideal solubility.

For very low ozone concentrations at -63° and -23° the solubility of ozone calculated by the formula $S_B^T(100\%) = S_B^T\frac{P_0 - P}{P(P_0 - 1)}$ is very close to the value calculated by the direct proportionality law $S_B^T(100\%) = SP\frac{1}{P}$, as Table 2 shows.

This is evidence that dilute solutions of ozone in Freons obey Henry's law. The solubility coefficients for ozone

TABLE 2. Calculated solubility values for ozone.

	$S_B^T(100\%) = S_B^T \frac{P_0 - P}{P(P_0 - 1)}$			$S_B^T(100\%) = S_P \frac{1}{P}$		
T, °C	CF-11	CF-113	CF-114	CF-11	CF-113	CF-114
—63	25.8	—	35	23.6	—	32
—23	6.6	9.4	—	6.6	9	—

TABLE 3. Solubility coefficient expressed in mole fraction.

T, °C	$X^{100\%}$			
	CCl_3F	CCl_2F_2	$CClF_3$	$CHClF_2$
—110	0.850	0.867	0.862	0.895
— 94	0.317	0.323		
— 63	0.084			
— 23	0.024			
	Ratio $\frac{X^{100\%}}{Xi}$			
—110	0.95	0.97	0.97	1.00
— 94	0.93	0.95		
— 63	1.01			
— 23	1.00			

($X^{100\%}$), expressed in mole fractions, are given in Table 3, together with the ratio of the real solubility to the ideal solubility Xi. It is clear that this ratio is close to unity, a rare occurrence in gas solubility.

From the data of Table 3, Chrétien and coworkers[9] have calculated the molar latent heat of dissolution of ozone in CCl_3F and CCl_2F_2, which turned out to be 3290 ± ± 50 and 3590 cal mole^{-1} respectively. The latent heat of evaporation of ozone is 3410 ± 100 cal mole^{-1} at the boiling point. These values are of the same magnitude, which suggests that no chemical reactions occur when ozone is dissolved in Freons, and that neither complexes nor solvates are formed.

Mahieux[10] also examined the possibility of obtaining mixtures of liquid and solid ozone with Freons, and measured the stability of these mixtures. The ozone was condensed in vessels of two types. One of the vessels (Fig. 7) is an ordinary spiral tube, fitted with a reservoir. The ozone–oxygen mixture obtained from the ozoniser is passed through the spiral cooled to about -140°. Only the ozone is liquified, and collects in drops in the reservoir, which already contains a known volume of condensed Freon. The alternative vessel (Fig. 8) includes a capillary through which the ozone–oxygen mixture is led into the condensed Freon, where the ozone condenses. It is best to use Freons CF-12 and CF-22 to condense the ozone. Freons having a boiling point lower than that of ozone are not recommended (for example, Freon-14). Freon-13 evaporates very rapidly under reduced pressure, entraining the ozone. The advantage of Freons CF-12 and CF-22 is that, because of their relatively high boiling point, the ozone evaporates first from the mixture. Also, the low melting point of these Freons (-158° and -181°) enables mixtures with solid ozone to be obtained at temperatures above the freezing point of ozone (-192.7°).

When ozone is condensed in Freon it forms a blue liquid which solidifies as the temperature is reduced to -192°, acquiring a transparent black colour if the molar concentration of ozone is ~60%. At lower ozone concentrations, liquid ozone and liquid Freon are miscible in all proportions without separating into layers. Layering occurs in

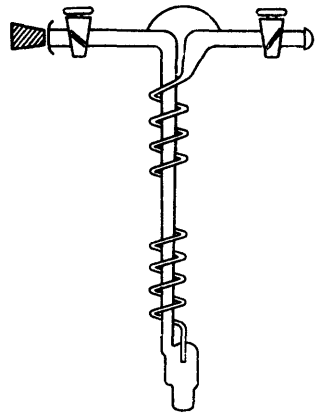


Fig. 7. Tube for liquefaction of ozone (with spiral).

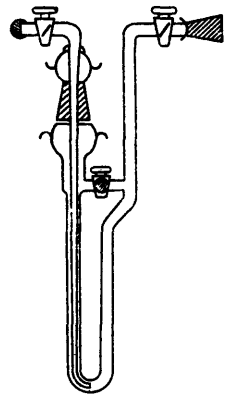


Fig. 8. Tube for liquefaction of ozone (with capillary).

the region from -230° to -270° for Freons CF-13, CF-12, and CF-22, but in practice the limiting temperature is that of liquid nitrogen (-196°), and therefore layering is not observed.

Streng and Grosse[18] have reported that ozone is unstable in the neighbourhood of its freezing point. Mahieux[10] showed that solutions of ozone in Freons are thermally stable, and that no explosive decomposition takes place when ozone is solidified in a Freon medium.

The condensation of ozone is more efficient than the dissolution process, since from 70 to 90% of the ozone passing through the Freon is retained by liquefaction as compared with 10–15% during dissolution. The concentration of ozone in ozone–Freon mixtures can reach 50%.

The preparation of solutions of ozone in Freons has practical importance[11]. The solubility of ozone in Freons enables ozone to be separated from oxygen and to be stored safely and for long times in a concentrated form: it offers a portable source of ozone which can always be handled and conveyed over any distance.

By evaporating ozone from these solutions we can obtain pure ozone or ozone mixed with oxygen or with inert gases

at a known concentration[12]. Various substances can be made to react directly with the ozone in an inert solvent medium[13].

Solutions of ozone may be stored in stainless steel bottles[11] of 5, 10, and 15 l capacity (calculated as 100% ozone). Below -50° these solutions may be stored indefinitely. At room temperature the decomposition time of the ozone (time for 50% decomposition of the stored ozone) is of the order of weeks. As a rule, vessels containing dissolved ozone are stored at -30° and transported at -15°. At the latter temperature the solutions can be kept for one month. The rate of decomposition of the ozone depends on the nature of the Freon and on the shape of the vessel. Solutions of ozone in Freon-12 have been examined for sensitivity towards mechanical, electrical, and explosive shocks, and for temperature resistance[19]. The sensitivity of both the vapour phase and the liquid phase of a 10% solution of ozone in Freon-12 towards a high-voltage electrical discharge and towards detonation at high pressures was tested. No detonation took place when explosion was initiated in the gas or the liquid phase of a 12% solution of ozone in Freon-12 at -78° and 105 atm (of helium). The gas and the liquid phase were tested for shock resistance by dropping a 5.6 kg weight from 35 cm, but it was found that solutions containing 10 wt.% of ozone in Freon-12 are completely safe at -78°. Experiments on the effect of temperature showed that increase in temperature does not produce an explosion, or even appreciable decomposition of the ozone.

We have recently confirmed[20] that solutions of pure ozone in Freon-12 and -113 can be prepared, and handled with safety during liquid-phase reactions with alkalis and peroxidic compounds.

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APPLICATION OF ELECTRON SPIN RESONANCE IN POLYMER CHEMISTRY

S.E.Bresler and E.N.Kazbekov

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Electron spin resonance (ESR) is the name given to the resonance absorption of the energy of an oscillating magnetic field by a paramagnetic substance in which the field induces transitions of unpaired electrons between split Zeeman levels. The ESR phenomenon was discovered by Zavoiskii[1] and interpreted theoretically for the first time by Frenkel'[2]. The ESR method is of particular value for the study of free radicals, because of its high sensitivity, the possibility of investigating free radicals directly in the course of reactions, and also the completeness and uniqueness of the information about their structure thus obtained. The number of ESR studies on free radicals is extremely large. In this review we shall confine ourselves to certain results relevant to the physics and chemistry of polymers.

I. THEORETICAL FOUNDATIONS OF THE ESR METHOD

1. The Basic Features of the Phenomenon

Consider a specimen containing unpaired electrons, for example a reaction mixture with free radicals. In the absence of an external magnetic field, all orientations of the spins and magnetic moments of the electrons have the same energies. An external magnetic field removes the degeneracy: only two orientations of the spins and magnetic moments of the electrons are now possible, along and against the field, since the electron spin is $S = 1/2$ and according to quantisation rules only $2S + 1 = 2$ states are possible. This means that the zero energy level splits into

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APPLICATION OF ELECTRON SPIN RESONANCE IN POLYMER CHEMISTRY

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I. THEORETICAL FOUNDATIONS OF THE ESR METHOD

1. The Basic Features of the Phenomenon

Consider a specimen containing unpaired electrons, for example a reaction mixture with free radicals. In the absence of an external magnetic field, all orientations of the spins and magnetic moments of the electrons have the same energies. An external magnetic field removes the degeneracy: only two orientations of the spins and magnetic moments of the electrons are now possible, along and against the field, since the electron spin is $S = 1/2$ and according to quantisation rules only $2S + 1 = 2$ states are possible. This means that the zero energy level splits into

two sublevels (Zeeman effect) and the electrons are distributed between these sublevels (Fig. 1) in accordance with the Boltzmann law:

$$\frac{n_1}{n_2} = e^{-\frac{\Delta E}{kT}}, \quad (1)$$

where n_1 and n_2 are the numbers of electrons in the upper and lower levels, ΔE is the energy difference between the levels, T is the absolute temperature, and k the Boltzmann constant. The magnitude of the Zeeman splitting is

$$\Delta E = g\beta H. \quad (2)$$

In this expression β is a Bohr magneton and g the spectroscopic splitting factor, which is 2.0023 for a "free" electron. For most of the radicals investigated, the g-factor differs only slightly from this value. If in addition to the permanent magnetic field H an oscillating magnetic field with frequency ν acts on the specimen such that

$$h\nu = g\beta H \quad (3)$$

and directed perpendicular to the permanent magnetic field, the electrons pass from the lower to the upper level with absorption of energy from the field. At the same time electron transitions from the upper to the lower level with emission of energy are induced. But, since according to Eqn. (1) the number of electrons n_2 in the lower level is higher than the number of electrons in the upper level, it follows that on average there will be more transitions per unit time from the lower to the upper level than in the reverse direction, i.e. the oscillating magnetic field will tend to equalise the populations of the levels and its energy will be absorbed.

At the same time there exist the so-called relaxation processes which tend to restore the initial "Boltzmann" distribution of electrons, whereby their excess energy is converted into thermal lattice vibrations (spin–lattice relaxation) or the energy is redistributed among the electrons themselves (spin–spin relaxation). The rates of these relaxation processes, which can be characterised by the corresponding relaxation times T_1 and T_2 (the times during which the excess energy decreases by a factor of e), determine the maximum intensity of the oscillating magnetic field for which the Boltzmann distribution is still maintained. If, as happens fairly frequently (for example in macroradicals in polymers), the relaxation times are relatively high, thermal equilibrium breaks down at relatively low intensities (of the order of 1 mV) and the energy absorbed by the specimen from the oscillating magnetic field ceases to be proportional to the incident energy (saturation effect). In the absence of saturation, the energy absorbed per unit mass of the paramagnetic substance is defined by the expression

$$P_\nu = \frac{\pi^2}{2} \frac{N_0 g^2 \beta^2}{3kT} S(S+1) H_\sim^2 \nu^2 I(\nu). \quad (4)$$

Here N_0 is the number of unpaired electrons per gramme of the substance, $H_\sim$ the amplitude of the oscillating magnetic field, and $I(\nu)$ a "function of the line form". This function takes into account the finite width of the paramagnetic absorption line and is normalised in such a way that $\int_{-\infty}^{+\infty} I(\nu)d\nu = 1$. Bearing in mind that for lines which are not too broad one can put with sufficient accuracy $\nu = \nu_{res}$, we obtain the following expression for the total integral energy absorbed by unit mass of the specimen with $S = 1/2$

$$P = \pi^2 \frac{N_0 g^2 \beta^2}{3kT} H_\sim^2 \nu_{res}^2 = \frac{\pi^2 g^4 \beta^2}{3kTh^2} H_{res}^2 H_\sim^2 N_0. \quad (5)$$

The condition of the absence of saturation can be written in the form

$$\frac{1}{4}\gamma^2 H_\sim^2 T_1 T_2 \ll 1 \quad (6)$$

where γ is the gyromagnetic ratio for the electron.

2. Parameters of the Spectral Line

Fig. 2 shows the variation of the energy of the oscillating magnetic field P absorbed by the paramagnetic specimen with the strength of the steady magnetic field H for a constant frequency of the variable magnetic field. This is the relation one has in mind when one speaks of the ESR "spectrum". Fig. 2 shows the singlet spectrum corresponding to the structure of the energy levels in Fig. 1. The ESR spectrum can be characterised by the following fundamental parameters: intensity, g-factor (or the resonance strength of the magnetic field H_{res}), and the width and form of the lines.

Intensity of the spectrum. The intensity of the ESR spectrum is understood as the area S under the curve describing the variation of the energy of the oscillating magnetic field absorbed by the specimen with the strength H of the steady magnetic field (Fig. 2). It follows from Eqn. (4) that, other conditions being equal, the intensity of the spectrum is proportional to the number of unpaired electrons per gramme of the test substance:

$$N_0 = \alpha S, \quad (7)$$

where α is a proportionality coefficient which depends on the units in which S is measured and on the parameters of

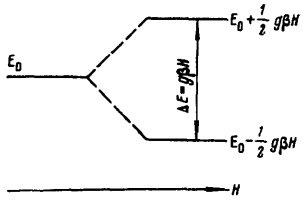


Fig. 1. Schematic representation of the Zeeman splitting of electronic levels.

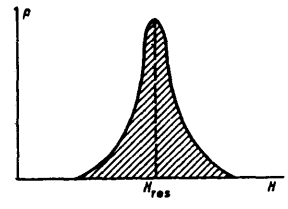


Fig. 2. A singlet ESR spectrum.

the measuring system. Thus if the coefficient α is known, the determination of the concentration of unpaired electrons in the specimen requires the experimental measurement of S. On the other hand, if α is unknown it is necessary to determine under identical conditions the values of S and S_{st} for the test specimen and a standard specimen with a known concentration N_{st} of unpaired electrons. Then the concentration of unpaired electrons in the test specimen is given by the expression

$$N_0 = N_{st}\frac{S}{S_{st}}. \quad (8)$$

The second method is in fact normally used in practice.

The g-factor. The g-factor is a measure of the contribution of the orbital magnetism to the total magnetic moment of the unpaired electron. The weaker is the interaction between the spin and the orbital momenta, the smaller is the difference between the g-factors of the paramagnetic substance under test and that of the free electron. As already stated, this is in fact what happens in free radicals. Since in most cases free radicals are complex asymmetric species, their orbital degeneracy is removed by the internal electric field, which arises from the surrounding atoms, and the orbital magnetism is greatly suppressed. For this reason, the spin–orbital coupling of the unpaired electron in free radicals is usually very weak. Only in rare cases does the g-factor of free radicals differ from that of the free electron by more than several thousandths (for example, $g > 2.01$ for radicals with an unpaired electron at a sulphur atom). On the other hand, in paramagnetic ions whose unpaired electrons belong to a deeply embedded d-shell, appreciable spin–orbital coupling is often observed. Since the g-factor can be determined with very high accuracy, its measurement can provide definite information about the magnitude of the spin–orbital coupling and can be used for the identification of free radicals.

It should be noted that, generally speaking, the g-factor is a tensor quantity. Therefore in single-crystal (or strongly oriented) specimens anisotropy of the g-factor can be sometimes observed. In other cases the anisotropy of the g-factor can cause some broadening of the resonance lines.

The form and width of the lines. The lifetime of unpaired electrons in the excited state, i.e. in the upper Zeeman level, determines the width of the ESR spectral line, in accordance with the uncertainty principle. The following fundamental processes determine the lifetime of excited unpaired electrons: (a) spin–lattice interaction; (b) spin–spin dipole interaction; (c) exchange interaction.

The transfer of energy from unpaired electrons to the molecules of the substance or to the lattice constitutes the basis of the mechanism of the *spin–lattice* relaxation. The coupling between the spin system and the lattice is magnetic (spin–orbital interaction). However, as already stated, the spin–orbital coupling in free radicals is weak. Therefore the spin–lattice relaxation time T_1 is relatively large (it can reach several seconds) and cannot make an appreciable contribution to the broadening of the resonance line. At the same time the large value of T_1 can in fact be responsible for the saturation effect.

Spin–spin interaction. Each unpaired electron in the constant external magnetic field H is acted upon, apart from the external field, by the local fields H_{loc} due to the magnetic moments of other electrons. The result is that the resonance condition (3) can be satisfied for individual unpaired electrons at various values of H, i.e. the resonance line is broadened. The strength of the local fields is inversely proportional to the cube of the distance between the unpaired electrons. Therefore spin–spin interaction increases with the concentration of unpaired electrons in the specimen and their interaction often in fact determines the width and form of the spectral lines. Two limiting cases of spin–spin interaction are possible.

a. The paramagnetic species are at large distances from one another and interact only during collisions, the duration of which is short compared with the periods between the collisions (this case obtains in gaseous and liquid phases at low concentrations of the paramagnetic species). The line form is then described by a Lorentzian curve:

$$I_L(H) = \frac{I_L(H_0)}{1+\left(\frac{H-H_0}{\Delta H_L}\right)^2}. \quad (9)$$

b. The paramagnetic species are in different quasi-steady-state local magnetic fields (solid phase, high concentration of paramagnetic species). In the absence of exchange interaction, the line form is in this case gaussian

$$I_G(H) = I_G(H_0)e^{-\frac{(H-H_0)^2}{\Delta H_G}}. \quad (10)$$

The characteristic line parameters ΔH_L and ΔH_G are related in the following way to the experimental line width $\Delta H_{1/2}$ at half the peak height:

$$\Delta H_L = 0.5\ \Delta H_{1/2};\quad \Delta H_G = \frac{1}{2\ln 2}\Delta H_{1/2}. \quad (11)$$

Exchange narrowing. If the local magnetic fields in which the paramagnetic species are situated change fairly rapidly, they become averaged out and line narrowing results. Such averaging out can be due to an exchange effect. The exchange effect arises when, as a result of their high concentration the electron clouds of the paramagnetic species begin to overlap. Extensive delocalisation of the unpaired electrons and rapid motion of the paramagnetic species can also lead to the averaging out of the local magnetic field. In all these cases the paramagnetic resonance lines become narrower in the central region, approaching Lorentzian line shape.

3. Hyperfine Structure (HFS) of the ESR Spectra

The hyperfine structure of the ESR spectra is due to the interaction of the unpaired electrons with the paramagnetic nuclei. According to the quantisation rules, the magnetic moment of a nucleus with a spin I has $2I + 1$ possible orientations relative to the external magnetic field. An additional magnetic field, set up by the nucleus at the location of the electron, has values corresponding to each of these orientations. Therefore each level is split into $2I + 1$ sublevels. The oscillating magnetic field does not give rise to reorientation of the nucleus, since its frequency does not correspond to resonance with respect to the nuclear transitions. Consequently the following selection rules operate for the electronic transitions: $\Delta M_I = 0$ and $\Delta S_Z = \pm 1$ (M_I is the nuclear magnetic quantum number and S_Z the projection of the electron spin in the direction of the field). As a result $2I + 1$ lines at equal distances appear in the spectrum. Fig. 3 shows as an example (in a schematic form) the splitting of the electronic levels in the interaction of an unpaired electron with a single proton ($I = 1/2$). It is seen

that a doublet is obtained instead of a singlet spectrum. In most modern ESR spectrometers the derivative of the absorption line with respect to the magnetic field (dI/dH) is recorded, rather than the line itself. For this reason, the spectral lines are of the form shown in the lower part of Fig. 3.

If the unpaired electron interacts with several magnetic nuclei, $\prod_r (2I_r + 1)$ lines of equal intensity appear in the spectrum (I_r is the spin of nucleus r). If the splitting due to different nuclei is such that the corresponding numbers of lines are integral multiples of one another, some lines overlap. The intensities of the components of such a spectrum bear simple multiple relations to one another. In practice, one frequently encounters the case where the interaction of an unpaired electron with several protons is the same. The number of lines in this spectrum is then $n + 1$ (where n is the number of protons) and the relative intensity of the kth line from the beginning of the spectrum is given by the coefficients of Newton's binomial:

$$C_n^{k-1} = \frac{n!}{(k-1)!\,(n-k+1)!}. \qquad (12)$$

Thus interaction with two protons gives rise to three lines with intensity ratios of 1 : 2 : 1 and interaction with three protons gives rise to four lines with intensity ratios of 1 : 3 : 3 : 1.

The interaction of electron spin with the magnetic moment of the nucleus consists of two parts[3]. The first part is analogous to the usual dipole–dipole interaction between two magnetic moments. This interaction depends on the direction of the external magnetic field relative to the radius vector joining the electron to the nucleus, and is therefore referred to as anisotropic. The second part is due to the isotropic contact interaction, which is independent of the direction and is proportional to the square of the modulus of the electronic wave function at the point where the nucleus is located.

Since the majority of free radicals have been investigated in the non-crystalline (or polycrystalline) state, the anisotropic interaction in them as a rule does not give rise to hyperfine structure, resulting only in the broadening of the spectral line. For this reason, the hyperfine structure of the spectrum of free radicals is usually caused by the isotropic interaction. This interaction is non-zero only when the density of the unpaired electron cloud is non-zero at the point where the nucleus is located. Only atomic s-orbitals or molecular σ-orbitals have a finite electron density at the nucleus and consequently can participate in the isotropic hyperfine interaction.

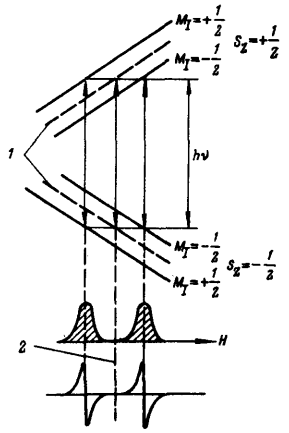


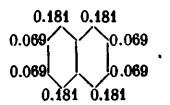
Fig. 3. Formation of the hyperfine structure of the ESR spectrum:
1) initial electronic levels; 2) position of the line in the absence of hyperfine splitting.

From this point of view, there should be no contact hyperfine interaction in aromatic free radicals, since the unpaired electrons in these radicals are located in π-orbitals with zero electron density in the plane of the ring where the hydrogen atoms are located. Nevertheless, the spectra of the majority of aromatic free radicals have a complex and highly resolved hyperfine structure. This can be understood within the framework of configurational interaction[4]. The result of such interaction is that a certain proportion of the excited σ-orbital state becomes combined with the purely π-orbital state of the electron. This leads to non-zero electron density in the plane of the ring and the appearance of hyperfine structure.

The hyperfine splitting ΔH can be calculated from the formula

$$\Delta H = Q\rho \qquad (13)$$

where Q is a constant (28 Oe for the aromatic CH bond) and ρ the unpaired electron density at the carbon atom to which the given hydrogen atom is joined. The distribution of electrons in conjugated systems between various carbon atoms is calculated by the usual methods of quantum chemistry — the valence bond or molecular orbital methods. We shall quote the distribution of electron density in the naphthalene radical-ion $C_{10}H_8^-$, which is a well-known initiator of anionic polymerisation. Calculation by the molecular orbital method yields the following distribution:



Consequently, theory predicts that, as regards their interaction with an unpaired electron, protons can be divided into two groups. Each group includes four protons and therefore a spectrum consisting of (4 + 1)(4 + 1) = = 25 lines may be expected, and is in fact observed experimentally.

In non-conjugated systems the principal mechanism of the interaction of the unpaired electron with hydrogen atoms is the so-called hyperconjugation. The phenomenon consists essentially in the overlapping of the orbitals of the radical π-electron with the electron clouds of other atoms. As a result, non-zero unpaired electron density can appear at the location of the nuclei of these atoms. For example, in ethyl radicals $CH_3-CH_2^{\cdot}$ the unpaired electron interacts not only with the two protons of the methylene group but also with the three protons of the methyl group. The spectrum of ethyl radicals produced on irradiation of ethane[5] shows that the unpaired electron interacts somewhat more strongly with the protons of the methyl group. This gives rise to a hyperfine structure of twelve lines (Fig. 4). The theory of hyperconjugation was developed by Mulliken and coworkers[6-9] and applied for the first time by McLachlan[10] to the calculation of ESR spectra. Vol'kenshtein and Milevskaya[11,12] used this theory to calculate the spectra of polymeric radicals. They obtained expressions



Fig. 4. ESR spectrum of the ethyl radical.

for the hyperfine splitting by the protons of the methyl and methylene groups joined to the carbon atom with the unpaired electron. When the possible conformations of the macroradicals and the statistical weights of these conformations are known, these expressions make it possible to estimate the hyperfine structure of the spectrum. Conversely, when a highly resolved structure of the ESR spectrum is available, it can be used to estimate the conformations of the radicals.

II. ELECTRON SPIN RESONANCE TECHNIQUE

The vast majority of the ESR spectrometers used nowadays operate in the ultrahigh frequency range, namely in the vicinity of 10^{10} c/s (wavelength 3 cm). The strength of the constant magnetic fields is then about 3000 Oe. Fig. 5 shows the block-circuit of an ESR spectrometer. The principal elements of this circuit are present in the majority of spectrometers, despite the wide variety of designs employed. A reflex klystron is normally used as a source of electromagnetic waves. The electromagnetic waves are conducted via a wave guide to a cavity resonator in which the test specimen is located. The frequency of the klystron oscillations is maintained to a high accuracy, with the aid of a special electronic circuit, at the value equal to the resonant frequency of the cavity. The resonator is positioned between the poles of a magnet (usually an electromagnet) in such a way that the ultrahigh frequency magnetic field in the specimen is perpendicular to the steady magnetic field.

The resonator is connected by a second wave guide to a crystal ultrahigh frequency detector. If the strength of the magnetic field is now altered, then under resonance conditions the ultrahigh frequency power dissipated in the resonator increases and a smaller power is applied to the detector. Various ways of recording the paramagnetic resonance signal are possible. In one of them the strength of the steady magnetic field is adjusted close to the resonance value and then an additional low-frequency magnetic field, whose amplitude greatly exceeds the width of the absorption line, is established in the gap of the magnet with the aid of special coils. This gives rise to a signal at the output from the detector corresponding to the form of the absorption line, at a frequency equal to twice the modulation frequency. After amplification with a broad-band amplifier, the signal can be detected on the oscilloscope screen. However, the need to use a broad-band amplifier in this method of signal detection greatly reduces the sensitivity of the spectrometer, because, in addition to the useful signal, the interfering noise signals which may originate from the klystron oscillator and the detector, are also amplified. Therefore this method can be used only when the test specimen contains a large number of free radicals.

If high sensitivity is required, another method of detecting the ESR signal is used. In this method the field of the electromagnet is varied linearly with time (Fig. 6) and passes through the resonance value. At the same time a radio-frequency magnetic field is set up with the aid of modulation coils. However, now its amplitude must be smaller than the width of the resonance line. It is readily seen that in this case we shall have at the output from the detector a variable potential with a frequency equal to the modulation frequency. This potential is amplified by a narrow-band resonance amplifier and is rectified with a phase-sensitive detector fitted with a very narrow-band filter. The form of the rectified signal corresponds to the first derivative of the absorption line. The signal is recorded with a pen recorder. The possibility of using very narrow-band filters (about 0.1 c/s) in this method of recording greatly increases the useful signal : noise ratio, since the noise is proportional to the square root of the transmission band width. The reduction of noise is also facilitated by the fact that a fairly high (up to 1 Mc/s) modulation frequency of the magnetic field is usually chosen.

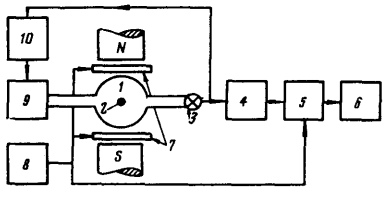


Fig. 5. Block-circuit of an ESR spectrometer:
1) cavity resonator; 2) specimen; 3) crystal detector; 4) amplifier; 5) phase-sensitive detector; 6) pen recorder; 7) modulating coils; 8) modulation generator; 9) Klystron; 10) AFC (automatic frequency control).

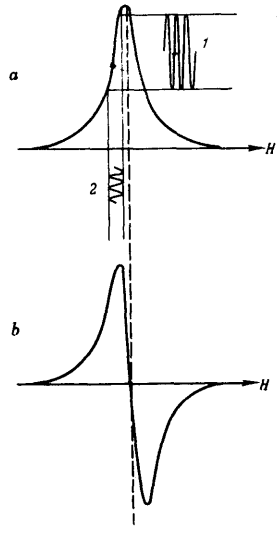


Fig. 6. Method using low amplitude modulation of the magnetic field:
1) resultant modulation of the ultrahigh frequency signal; 2) modulation of the magnetic field.

This makes it possible to avoid to a large extent the low-frequency noise from the crystal detector which occurs at the spectral density maximum. This spectrometer is one of the most widely used.

The type of resonator used in the spectrometer is determined by the specific features of the investigation. It is possible to use not only the transmission cavity shown in Fig. 5 but also a reflection cavity with an ultrahigh frequency compensating network. The superheterodyne method of signal detection is also employed, abeit much more rarely.

However, we shall not consider these problems in detail, the readers being referred to the appropriate literature [13,14]. In conclusion of this section we shall only mention that the maximum sensitivity of the existing spectrometers corresponds to 10^{-12}–10^{-13} mole of crystalline diphenylpicrylhydrazyl (DPPH) free radicals. But, since in most cases one deals not with crystalline materials but with solutions (or, for example, with polymerisation mixtures), greater interest attaches to concentration sensitivity, i.e. the minimum concentration of radicals which can be measured. Under most favourable conditions (specimen with small dielectric losses, correctly chosen relative dimensions of the resonator and specimen), the sensitivity corresponds approximately to 10^{-7} M for a spectral width of about 3 Oe.

III. INVESTIGATION OF FREE RADICALS BY THE ELECTRON SPIN RESONANCE METHOD

All studies on the electron spin resonance of free radicals can be divided into two large groups – the study of stable free radicals and the study of active intermediate radicals and reactions in which they participate.

1. Stable Free Radicals. Inhibition of Polymerisation

Apart from the naphthalene radical-ion discussed above, numerous stable and semistable radicals with a more or less complex system of conjugated bonds have been investigated: triphenylmethyl, semiquinones, $\alpha\alpha$-diphenyl-β-picrylhydrazyl, and many others. In recent years much attention has been given to the synthesis of polymers with a system of conjugated π-bonds. These polymers are organic semiconductors and frequently give a narrow singlet ESR signal.

Semistable and stable radicals are formed from radical reaction (oxidation and polymerisation) inhibitors. These are radicals derived from quinones and semiquinones, aromatic amines, aromatic nitro-compounds, and polycyclic hydrocarbons. The ESR method permits a quantitative approach to inhibition processes.

The study of the inhibition of polymerisation by this method [15] led to the discovery of a new important fact, namely that up to four inhibitor molecules are consumed and an equal number of stable radicals are formed for each active radical destroyed. This very large "stoichiometric coefficient", given by the expression

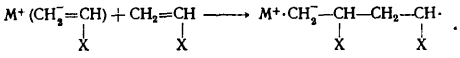
$$\frac{\text{number of inhibitor molecules consumed,}}{\text{number of deactivated radicals}}$$

implies that in the reaction of an active radical with an inhibitor molecule there forms initially a "hot" radical with an excess of vibrational energy, which is capable of further reactions with the monomer or other inhibitor molecules. Only after several such steps is the energy of the radicals reduced so much that they no longer initiate polymerisation. When an inert solvent is introduced into the system, the hot radicals are "cooled" as a result of collisions with solvent molecules and the stoichiometric coefficient tends to unity. The presence of hot radicals in polymerisation is evidence that energy chains can occur even in liquid-phase reactions.

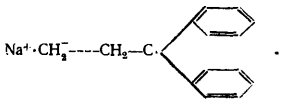
2. Active Free Radicals. Polymerisation

As already stated, the sensitivity of modern ESR spectrometers is in most cases insufficient to investigate free-radical reactions in the liquid phase. However, it proved possible with their aid to solve certain important problems of polymerisation theory. An example of this kind is the mechanism of the initiation of polymerisation by alkali metals.

The hypothetical polymerisation mechanism was as follows. A complex consisting of the monomer molecule and a metal atom (charge-transfer complex) attacks a new monomer molecule and gives rise to a radical-ion which subsequently either recombines at the radical centre or grows in two directions at once:



To confirm this mechanism, it was necessary to detect the free radicals in the polymerising system. This was done in the polymerisation of diphenylethylene under the action of metallic sodium [16]:



In this case the radical proved to be so stable that it did not recombine and chain growth took place at the anionic centre.

The classical examples of radical polymerisation could be investigated only under special conditions. In 1953 Bamford and Jenkins showed [17] that in the polymerisation of certain monomers, in which the polymers formed are insoluble, part of the macroradicals are captured by the precipitated gel and stabilised. The ESR spectra of such radicals in polyacrylonitrile were investigated by Bamford and coworkers [18].

In 1958 Ingram and coworkers [19] succeeded in investigating the spectra of many free macroradicals by adding a precipitant to the polymerisation system. Another method of producing a large number of macroradicals was used by Fraenkel et al. [20] and Atherton et al. [21] It consists in the addition to the system of a certain amount of a cross-linking agent. During polymerisation part of the radicals remain trapped in the three-dimensional network formed. Finally, the spectra of radicals trapped in poly(methyl methacrylate) and poly(vinyl acetate) after the onset of the so-called gel-effect in photopolymerisation have been investigated [20,22]. However, it has been shown [22] that the trapped radicals are a side-product of the reaction and their concentration is not directly related to the process kinetics.

O'Donnell et al. [23] investigated the solid-phase polymerisation of barium methacrylate dihydrate. Irradiation at -196° of a single crystal of barium methacrylate dihydrate

gives rise to a fully isotropic spectrum which is attributed to $(CH_3)_2\dot{C}COO^-$ radicals formed when hydrogen adds to the double bond of the methacrylate ion. When the specimen is heated to 20°, a new, anisotropic spectrum appears, with nine lines if the magnetic field is parallel to the *a* or *b* axes of the pseudo-orthorhombic crystal and with 13 lines if the field is parallel to the *c* axis. This spectrum is attributed to the radical of the growing chain:

$$RCH_2\dot{C}(CH_3)COO^-.$$

The anisotropic properties of the spectrum showed that the growing radicals have a definite crystallographic orientation, or, in other words, the distribution of the monomer molecules in the crystal lattice determines the position of the growing macroradical.

3. Macroradicals in Solid Polymers. Structure and Spectra

In 1951 Schneider and coworkers[24] observed the ESR spectrum of X-irradiated poly(methyl methacrylate). Their results and also subsequent studies showed that polymers are excellent media for the trapping of free radicals. The great advantage of polymeric matrices is the possibility of investigation of the radicals formed therein at relatively high temperatures (up to the softening temperature of the polymers), because of the powerful inhibition of the motion of the polymeric chains. This greatly extends the range of free-radical processes which can be studied by the ESR method, the polymer constituting an irreplaceable model system for the investigation of fundamental free radical reactions. A wide variety of methods for the preparation of radicals are used: radiolysis under the action of radiation of all types, trapping of free radicals in polymerisation processes, mechanical destruction of polymers.

The greatest number of studies on the electron spin resonance of irradiated polymers were undertaken to interpret the ESR spectra and to determine the structure of macroradicals. It can now be regarded as established[25-27] that, on irradiation of polyethylene at a low temperature, alkyl radicals are formed as a result of the scission of hydrogen atoms:

$$\sim CH_2-CH_2-\dot{C}H-CH_2-CH_2\sim.$$

Their spectrum consists of six lines corresponding to the interaction of the unpaired electron with one α-proton and with four β-protons. On raising the temperature (and also when the irradiation is carried out at room temperature), the spectrum disappears and the spectrum of another radical with an odd number of lines is observed. The latter is most likely due to radicals of an allyl type:

$$\sim CH_2-\dot{C}H-CH=CH_2\sim.$$

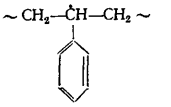
Such radicals are also produced as a result of the migration of the unpaired electron along the polymeric chain (via a consecutive relay-type transfer of hydrogen atoms) and its trapping by the double bond formed in consequence of radiolysis.

The ESR spectrum of the macroradicals in irradiated Teflon has also been investigated[28-20]. The spectrum is due to fluoroalkyl radicals:

$$\sim CF_2-CF_2-\dot{C}F-CF_2-CF_2\sim.$$

At room temperature the spectrum consists of ten lines due to the interaction of the unpaired electron with the fluorine atoms in the α- and β-positions. At a high temperature (250°) it is possible to observe an additional splitting caused by the interaction of the unpaired electron with the fluorine atoms in the γ-position.

The spectrum of free polystyrene radicals has been investigated in the course of the mechanical destruction of polystyrene in a vacuum[31,32] (Fig. 7). It consists of a poorly resolved triplet with a separation of 19 Oe between the components. Most probably this spectrum is due to radicals of the type



which can form as a result of the removal of hydrogen atoms from the polymeric chain by the more active primary radicals generated in the mechanical destruction of polystyrene. The hyperfine structure is formed as a result of the interaction of the unpaired electron with the protons of the neighbouring methylene groups. The non-equivalence of the protons (equivalent interaction of the unpaired electron with four protons would have given rise to a five-line spectrum) can be explained by the impossibility of free rotation of these groups about the C–C bonds. The relatively low extent of hyperfine splitting of the spectrum is due to the considerable delocalisation of the unpaired electron in the phenyl ring and the decrease of its density at the carbon atoms of the chain. Such delocalisation is possible if the plane of the ring coincides with the plane of the corresponding section of the chain. At the same time the electron density at the individual atoms within the ring is insufficient to give rise to additional lines and is responsible only for a certain broadening of the main lines. It is interesting that the hyperfine splitting in the spectrum of radicals generated in the mechanical destruction of isotactic polystyrene[31] is 34 Oe. This difference can be explained by the fact that the phenyl rings in isotactic polystyrene lie in planes almost perpendicular to the main chain and therefore they cannot withdraw the unpaired electron by conjugation. The ratio of the extents of splitting in the spectra of atactic and isotactic polystyrene is in good agreement with the ratio of the unpaired electron densities at the α-atom of the polystyrene radical calculated by the molecular orbital method for parallel and perpendicular orientations of the phenyl ring[12].

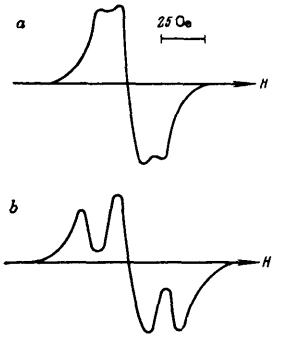


Fig. 7. ESR spectra of polystyrene macroradicals:
a) atactic polystyrene; *b*) isotactic polystyrene.

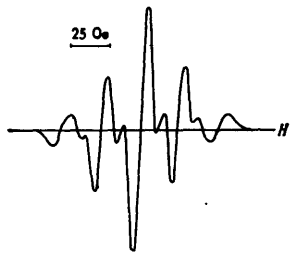
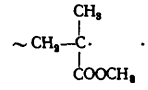


Fig. 8. ESR spectrum of poly(methyl methacrylate) macroradicals.

Fig. 8 shows the spectrum of the macroradicals in poly(methyl methacrylate). It is of the same form regardless of the methods of obtaining the radicals and is a result of the superposition of two series of hyperfine structure lines, a quintuplet and a quadruplet, with binomial intensity distributions in each series. The distances between the neighbouring lines in both series are the same and equal to 26 Oe. The centres of these spectra coincide, so that the quadruplet lines are located in the gaps between the quintuplet lines.

In 1958 Ingram et al.[19] and Abraham et al.[33] put forward the hypothesis that the ESR spectrum of poly(methyl methacrylate) is due to growing polymeric chain radicals:



The presence of two series of lines in the spectrum is then explained by the existence of definite conformations of these radicals, arising because of the impossibility of free rotation of the methylene group. In one of the conformations both protons of the methylene group are close to the nodal plane of the π-electron cloud of the unpaired electrons, interacting only weakly with the latter. This conformation corresponds to the quadruplet spectrum, which reflects the equivalent interaction of the unpaired electron with the three protons of the methyl group. In the other conformation one of the protons of the methylene group is located close to the meridian plane of the unpaired electron cloud and interacts with the latter in the same way as the protons of the methyl group. The four protons give rise to the quintuplet. On the other hand, the second proton of the methylene group interacts only very weakly with the unpaired electron. This hypothesis was subsequently confirmed in experiments on deuteriated derivatives of poly(methyl methacrylate)[34,35]. When both hydrogen atoms of the methylene group are replaced by deuterium atoms, only the quadruplet series remains in the ESR spectrum. This is explained by the fact that the hyperfine structure associated with deuterium atoms is usually unresolved. For this reason, the replacement of a hydrogen atom by deuterium is equivalent to the elimination of this atom from participation in the generation of the hyperfine structure. The quadruplet spectrum remaining after the substitution of the hydrogen atoms of the methylene group by deuterium corresponds to the interaction of the unpaired electron with the protons of the methyl group. When the protons of the methyl group are replaced by deuterium, there remains only a doublet spectrum corresponding to the interaction of the unpaired electron with one of the protons of the methylene group. Recently Fischer[36] investigated the polymerisation of methyl methacrylate in aqueous emulsion and established that the spectra produced in this process consist of the familiar groups of four and five lines, but each of these lines is in turn split into several further lines. This is probably due to the fact that, when the spectra of radicals in the liquid phase are observed, it is possible to achieve the resolution of the additional splitting by the protons of the methylene group, which in the solid phase is masked as a result of the line broadening caused by the anisotropic interaction.

IV. REACTIONS OF MACRORADICALS IN POLYMERS

1. Destruction of Macroradicals

The processes involved in the destruction of macroradicals in polyethylene after radiolysis were studied by several groups of investigators. In all these experiments it was established that the alkyl radicals are rapidly destroyed on raising the temperature of the specimen, while the destruction of the allyl radicals is very much slower. The kinetics of the destruction of radicals proved to be different in the experiments of various workers. Thus Lawton et al.[27] found that the kinetics of the destruction of alkyl radicals is consistent with a first-order equation. Charlesby et al.[37] observed the destruction of alkyl radicals according to a bimolecular law. Cracco et al.[38] established that alkyl radicals recombine according to a first-order law but with two different rate constants. On the other hand, allyl radicals are destroyed by a process which is neither of first nor of second order according to Charlesby et al.[37] and which is of first order according to Lawton et al.[27] Lawton[27] explains the kinetics of radical destruction (which he observed) as a result of the non-uniform distribution of the radicals in space. Charlesby et al.[37] suggest a uniform distribution of radicals and believe that a mechanism involving the migration of the radical state along the chain is responsible for their destruction.

The reason for the differences between the rates of destruction of radicals in the studies quoted above should probably be sought in the differences between the polyethylene specimens investigated (for example, it has been established[37] that the rate of destruction of alkyl radicals in specimens of low-pressure polyethylene is much higher than in high-pressure polyethylene). Possibly this is the explanation of the different kinetics of the destruction processes.

The recombination of radicals in Teflon has been investigated in detail by Tsvetkov et al.[39], who studied the recombination of both the initial fluoroalkyl radicals and the peroxy-radicals produced in the interaction between the initial radicals and oxygen. They established that the recombination in Teflon can be described by the usual bimolecular law, assuming that the recombination rate constant in the amorphous phase is higher than in the crystalline phase (specimens of different degrees of crystallinity were investigated). The recombination rate constants were determined from the rates of recombination of the peroxy- and fluoroalkyl radicals.

Ohnishi and Nitta[40] studied the destruction of radicals in irradiated poly(methyl methacrylate). They established that several hours after the beginning of the reaction the bimolecular law comes to hold exactly for the destruction of

radicals. On the other hand, in the first few hours deviations from the second-order law are observed. Shida et al.[41] investigated the destruction of radicals in irradiated poly(methyl methacrylate) during the initial period (up to 20 min) and found that the destruction of radicals is governed by a monomolecular law. Ohnishi and Nitta[40] determined the activation energy for radical recombination, which proved to be 28 kcal mole^{-1}. They believe that the radicals recombine as a result of the rotation of molecular segments, the activation energy for which has the same value[42]. Ohnishi and Nitta[40] found that the destruction of radicals is accelerated by oxygen, but failed to explain this phenomenon.

The recombination of macroradicals in γ-irradiated poly(vinyl chloride) has been investigated by Kuri et al.[43] and also by Egorova et al.[44] In both studies it was established that the destruction of radicals proceeds according to a second-order law with an activation energy of 38 kcal$\times$ $\times$ mole^{-1} [43] or 44 kcal mole^{-1}.[44] Like Ohnishi and Nitta[40], Kuri et al.[43] noted that oxygen accelerates the destruction of radicals.

It is noteworthy that in all the studies examined (with the exception perhaps of the work of Charlesby et al.[37]) it was assumed that the destruction of radicals in polymers occurs in the course of the collision during the rotation or displacement of smaller or larger sections of the polymeric chains. However, analysis of the available data[45,46] on the diffusional mobility of polymeric molecules shows that the idea of the interaction of macroradicals via collisions is inapplicable to the solid phase. Furthermore, the mechanism of the destruction of free radicals in polymers involving simply their collision as a result of mechanical displacement cannot account for the accelerating effect of oxygen on the destruction of macroradicals and the different rates of destruction of peroxy- and hydrocarbon radicals. Therefore it must be assumed that a different mechanism of the interaction between radicals obtains in polymers. Such mechanism is migration of radical states, whose existence has been established by Bresler et al.[32] This mechanism consists in the removal by the macroradicals of hydrogen atoms from the neighbouring chains, which results in the migration of the radical centre within the polymer. Such migration continues until two radical centres collide and annihilate one another by recombination or disproportionation. These workers investigated the destruction of macroradicals produced in the mechanical breakdown of polystyrene, poly(methyl methacrylate), and poly(vinyl acetate). The experiments showed that the destruction of radicals in the initial stages of the process is fully consistent with bimolecular kinetics and the reaction rate constants determined from the kinetic curves are consistent with the Arrhenius equation. The rate constants for the destruction of macroradicals are listed in Table 1.

It is noteworthy that the constants listed in Table 1 were determined with an accuracy limited by a factor having the dimensions of volume. The explanation is that, as shown by experiments on the reactions of macroradicals produced in the mechanical degradation of polymers by various gaseous agents, these radicals are not distributed uniformly throughout the bulk of the polymer, but are concentrated in a thin surface layer whose thickness is unknown. When oxygen is admitted into the tube containing the particles of the polymer with the macroradicals, the radicals are oxidised at a very high rate and are converted into peroxy-radicals with a characteristic asymmetric spectrum (Fig. 9). At temperatures below -50° the number of peroxy-radicals does

TABLE 1.

Polymer	$K = k/V$, mole^{-1} s^{-1}
Poly(methyl methacrylate)	$10^{18} \exp [(-29000 \pm 2000)/RT]$
Poly(vinyl acetate)	$10^{20} \exp [(-23000 \pm 1000)/RT]$
Polystyrene	$10^{20} \exp [(-24000 \pm 2000)/RT]$

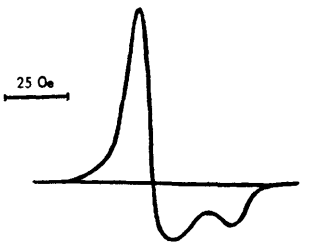


Fig. 9. ESR spectrum of peroxy-macroradicals.

not change at an appreciable rate. On raising the temperature, they begin to interact and disappear many times faster than the radicals with an unpaired electron at a carbon atom. In this case the equation for bimolecular kinetics is fully satisfied. The rate constants for the destruction of the peroxy-radicals are listed in Table 2.

It is seen that in polystyrene, for example at 20°, the peroxy-macroradicals disappear one thousand times faster than the intrinsic macroradicals of polystyrene. This is irreconcilable with the explanation of the radical destruction by collisions, because it is clear that the mechanical mobility of the initial and peroxy-radicals is identical. From the standpoint of the hydrogen removal process, the entire picture is clear: the primary radicals are relatively inactive and remove hydrogen from the neighbouring chains with difficulty. On the other hand, the peroxy-radicals are very reactive in the hydrogen removal step. There is yet another observation confirming the mechanism involving the migration of radical states. If after complete oxidation of the initial radicals the pressure of oxygen is reduced, the rate of destruction of radicals falls. At first sight this finding appears to be extremely surprising, because it would appear that molecular oxygen can have no influence on the behaviour of peroxy-radicals. However, from the standpoint of the radical state migration mechanism this phenomenon is quite natural. If there were no excess of dissolved oxygen in the polymer, the migration process would come to a stop when the peroxy-radicals became converted into secondary hydrocarbon radicals. No further reaction would then occur. On the other hand, when the system contains oxygen, the latter again adds to the new radical, removes hydrogen once more, etc. until two radicals annihilate one another as a result of a random

TABLE 2.

Polymer	$K = k/V$, mole^{-1} s^{-1}	Oxygen pressure, mmHg
Poly(methyl methacrylate)	$10^{21} \exp [(-23000 \pm 500)/RT]$	760
Poly(vinyl acetate)	$10^{14} \exp [(-14500 \pm 500)/RT]$	760
Polystyrene	$10^{15} \exp [(-12000 \pm 500)/RT]$	760
Polystyrene	$10^{14} \exp [(-12000 \pm 500)/RT]$	0.1

encounter. Thus the relay-type hydrogen transfer process is accompanied by chain oxidation of the polymer:

$$R\cdot + O_2 \rightarrow RO_2^{\cdot};\ RO_2^{\cdot} + R'H \rightarrow ROOH + R'\cdot;\ R'\cdot + O_2 \rightarrow R'O_2\cdot$$

and so on. The accumulation of peroxides in the polymer was confirmed by a special experiment.

2. Oxidation

The possibility of studying the reactions of macroradicals in polymers with various gaseous agents was demonstrated in several investigations. Thus Kuri and Ueda [47] studied the effect of sulphur dioxide on the radicals of various irradiated polymers. Kuri et al. [43] established that gases such as H_2S, NO, NO_2, and I_2 very rapidly destroy the radicals in irradiated poly(vinyl chloride), while hydrogen and sulphur dioxide do not react with the radicals. In another study Kuri et al. [48] observed the reactions of various gases with radicals in irradiated acrylamide and methacrylamide. The reactions of polymeric radicals with various gaseous agents were studied by Tsvetkov et al. [49]; they investigated the oxidation of fluoroalkyl radicals and their interaction with hydrogen and nitric oxide.

Several typical reactions, such as oxidation, removal of hydrogen, and the addition of monomers, were studied by Bresler et al. [50] In this investigation macroradicals were produced by mechanical destruction of polystyrene, poly(methyl methacrylate), and poly(vinyl acetate). The oxidation of radicals was studied at an oxygen pressure of 760 mmHg and at low temperatures. The kinetics of the process were followed by observing the increase of the intensity of the spectrum due to peroxy-radicals. In order to separate the overlapping spectra of the peroxy-radicals and the initial hydrocarbon radicals, the experiments were performed at a relatively high level of microwave power in the cavity (about 25 mV). Under these conditions strong saturation of the spectra of the primary radicals takes place, so that they are virtually undetectable and the spectra of the peroxy-radicals, which are saturated to a much smaller extent, are observed against what is virtually a zero background. The kinetics of the oxidation reaction are satisfactorily consistent with a monomolecular law, showing that the radicals are located in the immediate vicinity of the surface formed on breakdown of the polymers. Table 3 presents the oxidation rate constants calculated from the experimental data. It should be borne in mind that such determination does not yield the true oxidation rate constant but the product of the constant and the concentration of oxygen. Since on changing the temperature the concentrations of adsorbed and desorbed oxygen also change, the dissolution and adsorption of oxygen in polymers were studied and the temperature variation of the concentration of sorbed oxygen was determined [51] in order to find the true oxidation rate constant. The true constants k for the oxidation of polymeric radicals were determined by dividing the experimental constants K by the concentration of oxygen $[O_2]$.

3. Removal of Hydrogen

The next type of reaction which has been investigated is the abstraction of hydrogen by macroradicals. Cumene was used as the hydrogen donor. When cumene vapour is admitted into the tube with the specimen containing free radicals, the intensity of the spectrum due to the initial radicals decreases. A new spectrum does not appear because the low-molecular cumenyl radicals formed in this reaction rapidly recombine. Since the diffusion coefficients of cumene in polymers are very low, it was to be expected that the reaction of radicals with cumene would occur only on the surface of the polymer. Indeed experiment shows that the destruction of radicals is entirely consistent with monomolecular kinetics. The rate constants K calculated from the experimental data are presented in Table 4.

If the cumene adsorption constants are taken into account, the true constants k for the removal of hydrogen are obtained (last column of Table 4). In the temperature range investigated polystyrene radicals do not react with cumene at an appreciable rate. This finding may appear surprising, since, judging from the activation energies for the recombination and oxidation of radicals, polystyrene radicals should be no less active than the other radicals investigated. Thus we see that there is no direct correlation between the activity of the radical in a given reaction and the corresponding activation energy. This is because the preexponential factor, which can vary markedly from radical to radical, is no less rate-determining than the activation energy. Indeed, if, for example, we calculate the exponential terms in the rate constant expressions for the reactions of poly(methyl methacrylate) and poly(vinyl acetate) radicals with cumene at 250°K, we find that they differ only by a factor of 50. At the same time, the preexponential factors for these constants differ by a factor of 10^5.

4. Monomer Addition Reaction

The addition of the methyl methacrylate monomer to the macroradicals in polystyrene and poly(vinyl acetate) has been investigated. When the monomer vapour at a pressure of 10 mmHg is admitted into the tube containing a specimen of the ruptured polymer, the spectrum of the initial methyl methacrylate radicals changes at a very high rate (close to room temperature). The kinetics of the process were followed in this case by observing the increase in the intensity of the new spectrum, since it is much broader than the spectrum of the initial radicals and the extreme lines of its hyperfine structure do not overlap with the initial spectral lines, which makes it possible to separate the spectra of methyl methacrylate and other radicals. Here too the shape of the kinetic curves is entirely consistent with monomolecular kinetics and the temperature variation of the reaction rate constants agrees with the Arrhenius law. The rate constants K are listed in Table 5, which also includes the constants determined taking into account the monomer adsorption constants.

TABLE 3.

Polymer	$K = k[O_2]$, s^{-1}	k, $cm^3\ s^{-1}$
Poly(methyl methacrylate)	$20 \exp[(-4000 \pm 200)/RT]$	$6.0 \cdot 10^{-13} \exp[(-7900 \pm 500)/RT]$
Poly(vinyl acetate)	$3 \exp[(-2000 \pm 200)/RT]$	$1.6 \cdot 10^{-15} \exp[(-5900 \pm 500)/RT]$
Polystyrene	$0.2 \exp[(-1200 \pm 200)/RT]$	$4.0 \cdot 10^{-17} \exp[(-5300 \pm 500)/RT]$

TABLE 4.

Polymer	$K = k$[cumene], s^{-1}	k, $cm^3\ s^{-1}$
Poly(methyl methacrylate)	$2 \cdot 10^8 \exp[(-13000 \pm 1000)/RT]$	$2 \cdot 10^4 \exp[(-38000 \pm 1500)/RT]$
Poly(vinyl acetate)	$3 \cdot 10^{10} \exp[(-16000 \pm 1000)/RT]$	$2 \cdot 10^9 \exp[(-36000 \pm 1500)/RT]$

TABLE 5.

Polymer	$K = k[\text{monomer}]_0$, s^{-1}	k, $cm^3\ s^{-1}$
Poly(vinyl acetate)	$3 \cdot 10^{13} \exp[(-22000 \pm 1000)/RT]$	$10^{13} \exp[(-35000 \pm 1500)/RT]$
Polystyrene	$2 \cdot 10^{13} \exp[(-7500 \pm 500)/RT]$	$2 \exp[(-19800 \pm 1000)/RT]$

5. Some Problems of the Reactivity of Macroradicals

In the examination of the experimental data obtained[32,50] attention is drawn to the high activation energies for the reactions investigated compared with those for reactions in gas or liquid phases. Indeed the recombination of radicals in gas and liquid phases involves very low (virtually zero) activation energies. On the other hand, the activation energies found for macroradical destruction processes in solid polymers exceeds 20 kcal $mole^{-1}$. The reaction involving the removal of hydrogen by macroradicals may be compared with the chain transfer reaction in polymerisation. However, the activation energy for chain transfer in liquid-phase radical polymerisation of vinyl monomers is on average 10–15 kcal $mole^{-1}$, i.e. lower by a factor of more than two than the experimental activation energies for the reactions of macroradicals with cumene. The same may be said of the monomer addition reaction: the analogous chain growth reaction in polymerisation involves much smaller activation energies.

We shall now examine the problem of the absolute rate of destruction of macroradicals which should obtain on the basis of the radical state migration mechanism. For a free radical to be capable of removing a hydrogen atom from a neighbouring unit of the polymeric chain, it must first of all migrate over a distance δ separating it from this unit, i.e. on average over a distance of 3–5 Å (cross-sectional diameter of the polymeric chain). The time required for this is given by the formula

$$\tau = \tau_0 \exp(E_m/RT) \tag{14}$$

where E_m is the activation energy for the migration of the radical centre and the preexponential factor $\tau_0 = h/kT$ (h is the Planck constant, k the Boltzmann constant, and T the absolute temperature). Consequently, the frequency of the collisions of the given radical with hydrogen atoms is

$$\nu = \frac{1}{\tau} = = \frac{kT}{h} \exp(-E_m/RT). \tag{15}$$

However, each collision does not of course lead to the removal of hydrogen. The frequency of effective collisions, i.e. those which can lead to the removal of hydrogen atoms by the radical, is evidently

$$\nu_{eff} = \nu e^{\frac{-E_1 + S_1 T}{RT}} \tag{16}$$

where E_1 is the activation energy and S_1 the entropy of activation in the hydrogen removal reaction.

The average rate of movement of the radical centre is in this case

$$V = \delta \nu_{eff} = \delta \frac{kT}{h} e^{S_1/R} e^{-\frac{E_m + E_1}{RT}}. \tag{17}$$

Hence we find that the number of collisions of radical centres with each other per unit time is

$$N = V \sigma n^2 = \frac{\delta kT}{h} e^{S/R} e^{-\frac{E_m + E_1}{RT}} \sigma n^2 \tag{18}$$

where σ is the effective cross-section for the collision of two radical centres, and n the number of radical centres per unit volume. Knowing the number of collisions, we can express the rate of the bimolecular recombination or disproportionation reaction in the form

$$-\frac{dn}{dt} = N e^{S_2/R} e^{-E_2/RT} \tag{19}$$

where S_2 is the entropy of activation in the reaction of radicals with one another and E_2 the activation energy for this reaction. On combining Eqns. (18) and (19), we obtain finally

$$-\frac{dn}{dt} = A e^{\frac{S_1 + S_2}{R}} e^{-\frac{E_m + E_1 + E_2}{RT}} n^2. \tag{20}$$

Thus we see that the measured activation energy is the sum of the activation energies for three processes. In order to determine the activation energy for the intrinsic macroradical recombination process, it is necessary to subtract from the experimental value the activation energies for the migration of the radical centre and for the removal of hydrogen. The first of these energies probably does not differ markedly from the activation energy for the diffusion of low-molecular substances in polymers, say the monomer, i.e. is 13–15 kcal $mole^{-1}$. The activation energies for the removal of hydrogen should probably be the same as those for chain transfer in polymerisation, i.e. about 10–15 kcal $mole^{-1}$. Thus the sum of these two activation energies is 23–30 kcal $mole^{-1}$. We see that these values are very close to the experimental activation energies for the destruction of the initial hydrocarbon radicals. Hence follows the conclusion that the activation energy for the intrinsic macroradical recombination process is virtually zero, in complete agreement with all data on the recombination of radicals in gas and liquid phases.

It is readily seen that, for reactions of macroradicals with various reagents, the diffusion coefficients of the low-molecular reagents in the solid polymers should be included as multipliers in the rate constants for the reactions†. This is clear from the following considerations. Diffusion in solids is known[52] to be effected by successive jumps of the molecules (or atoms) between certain equilibrium positions. Suppose that the residence time of the molecules of the low-molecular reagent in an equilibrium position is τ and the distance between two neighbouring equilibrium positions is δ. Then the average rate of migration of these molecules is

$$\bar{u} = \delta/\tau \tag{21}$$

and the number of binary collisions of the reagent molecules with free radicals per second is

$$N = \bar{u} \sigma [R][C] \tag{22}$$

where σ is the effective collision cross-section and [R] and [C] are the concentrations of the radicals and the reagent molecules. According to Frenkel'[52], the diffusion coefficient can be expressed as follows in terms of δ and τ:

$$D = \frac{\delta^2}{\tau}. \tag{23}$$

† It must be emphasised that what is meant here is not the diffusion of these molecules from outside into the polymer but their thermal motion within the surface layer, which is so thin that the time required for the attainment in it of a steady-state concentration of the reacting molecules is much smaller than the reaction time.

From the last three equations, we obtain for the number of binary collisions the expression

$$N = A_1 D [R] [C]. \quad (24)$$

Hence the reaction rate constant can be written thus:

$$k = A_1 D e^{-\frac{\epsilon}{RT}} \quad (25)$$

where ϵ is the activation energy for the reaction. However, the diffusion coefficient D also depends on temperature:

$$D = D_0 e^{-\frac{E}{RT}}. \quad (26)$$

Here E is the activation energy for the diffusion process. On substituting Eqn. (26) in Eqn. (25), we obtain the final expression for the reaction rate constant:

$$k = A_2 e^{-\frac{E+\epsilon}{RT}}. \quad (27)$$

Thus the experimental activation energy is essentially the sum of the activation energies for the intrinsic reaction of the radical with the reagent molecule and for the diffusion of the latter. Table 6 presents the values for monomer addition reactions obtained by subtracting from the experimental activation energies (Table 5) the activation energies for the diffusion of the monomer in polymers.

It is seen that the activation energies thus obtained are very close to the values known for liquid-phase reactions. This is evidence in favour of the validity of the hypothesis concerning the effect of diffusion on the rate of reaction.

On the basis of the data presented, one may arrive at certain conclusions concerning the relative reactivity of macroradicals in oxidation, hydrogen removal, and double bond opening reactions. Data on the interaction of macroradicals with cumene and methyl methacrylate show that the activation energy is not a fully comprehensive characteristic of the reactivity of free radicals. The preexponential factor is often decisive.

From the standpoint of the theory of absolute reaction rates, the difference in the reactivities of radicals is explained by the difference in the free energies of the active complexes. The free energy, which comprises the energies of the atoms combined in the molecule minus the molecular entropy multiplied by the absolute temperature, can in fact serve as a true measure of the activity of a particular radical. It is by no means surprising that, on transition to the active-complex state, the number of degrees of freedom of a system consisting of a radical and molecule which it is attacking can change significantly, if only because such attack presupposes a highly specific mutual disposition of the two species. This means that there is also a marked change in the entropy of the system, i.e. ultimately considerable deviations of the preexponential factor from the value predicted by the collision theory are obtained. It is remarkable that a phenomenon similar to that described above is also observed in the usual radical polymerisation. Table 7 presents data on chain propagation rates in the polymerisation of certain vinyl monomers. The data were taken from Bengough and Melville[53].

TABLE 6.

Polymer	E, cal mole^{-1}
Poly(vinyl acetate)	11000±2000
Polystyrene	6800±1000

TABLE 7.

Monomer (T = 30°)	Rate constant, litre × mole^{-1} s^{-1}	E, kcal mole^{-1}	Preexponential factor $10^7 A$, litre × mole^{-1} s^{-1}
Vinyl acetate	1240	7.3	24.0
Styrene	55	7.8	2.2
Methyl methacrylate	143	6.1	0.5
Methyl acrylate	720	7.1	10.0

It is seen that, within the vinyl series alone, the absolute rates of chain propagation can vary by a factor as large as 25 (vinyl acetate–styrene). At the same time, the activation energies are almost identical. This implies that all the differences are due to the steric factor, i.e. the steric conditions which obtain when the macroradical approaches the monomeric molecule.

The macroradicals which have been investigated by the present authors can be arranged in the same activity series as regards the monomer addition and oxidation reactions: vinyl acetate, styrene, methyl methacrylate. In the reaction involving the removal of hydrogen from cumene the activity series changes, since styrene proves to be virtually inert at the temperatures investigated.

V. MACRORADICALS IN THE MECHANICAL DEGRADATION OF POLYMERS

In 1959 Bresler et al.[31] observed for the first time by the ESR method the free radicals which are generated in polymers on their mechanical breakdown. Subsequently this method of producing radicals in polymers was used by other workers[54,55]. The ESR study of the free radicals produced in the mechanical breakdown of polymers will undoubtedly play a major role in the elucidation of the physics of mechanical action on polymers themselves. Thus Zhurkov et al.[56] investigated the radicals produced on unidirectional compression of ebonite and their accumulation as deformation increases. When the deformation is relaxed, the number of radicals falls. The study of radicals produced on stretching Kapron‡ fibres[57] revealed a considerable similarity between the radical accumulation curves and the creep curves for the material, which indicates a relation between the creep and the number of ruptured chemical bonds.

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‡ Material similar to Nylon produced in the USSR (Ed. of Translation).

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DERIVATIVES OF STEROIDS WITH CONDENSED HETEROCYCLES

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1. INTRODUCTION

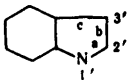
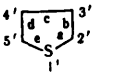
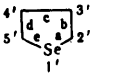
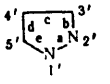
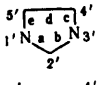
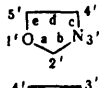
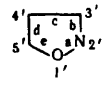
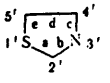
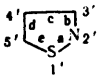
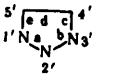
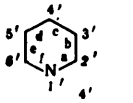
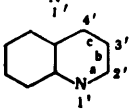
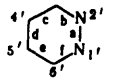
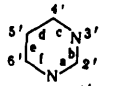
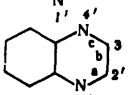
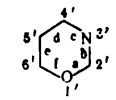
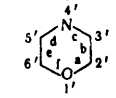
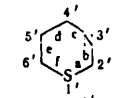
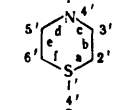
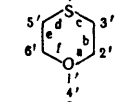
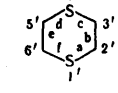
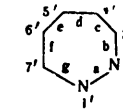
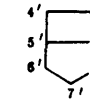
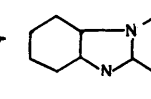
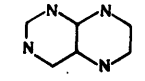
The study of structural modification of steroidal compounds, the scope of which is unequalled in any other branch of medical chemistry, has the aim of finding more active and more specific steroidal pharmaceutical preparations, free from harmful side action. Among the many known analogues of the steroids a special place is occupied by heterocyclic derivatives, the synthesis of which is linked with the hope of obtaining compounds which exhibit instead of the ordinary hormonal action completely different types of physiological activity — anabolic, anti-inflammatory, hypotensive, anti-tumour, etc.

The heterocyclic derivatives of steroids can be divided into two groups, the first of which includes compounds containing the heteroatom in the constitution of the cyclopentanoperhydrophenanthrene skeleton, and the second are the steroids with the normal carbon skeleton and heterocyclic substituents connected with it in some manner or other. The present review considers steroids of the second group which contain heterocyclic systems with N or S atoms condensed with the steroid skeleton and having not less than two C atoms in common with it. Only two brief reviews [1,2] have been published on this subject, and they do not adequately represent the experimental information that has been amassed.

At present there is no generally accepted nomenclature for heterocyclic derivatives of steroids. A simplified nomenclature is usually employed, with allowance for the steroidal nature of the compounds, since the rational nomenclature for condensed heterocyclic systems is much more complex. However, some authors take the steroid skeleton as the base component, others the heterocyclic ring. Thus, compound (I) is named [4,3-*b*]pyrazoloandrostane (as in the present review†), or pyrazolo[4,3-*b*]androstane, or, finally, androstano[3,2-*c*]pyrazole. In addition to the index of the bond, the mutual arrangement of the steroidal skeleton and the heterocycle can be denoted also by the numbers of the atoms; according to this system compound (I) can be named pyrazolo[3′,4′–3,2]androstane. There are also differences in the finer details of nomenclature. For example, in the Italian literature compound (I) is named as a derivative of 1′-methylandrostano[3,2-*c*]-pyrazole, but compound (II) as a derivative of 1′-methylandrostano[2,3-*d*]pyrazole [2]; at the same time most authors

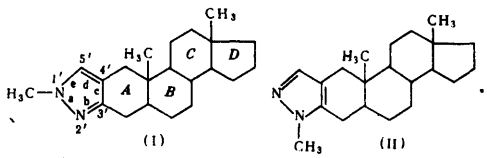
† There are, however, a number of errors and inconsistencies in the Russian text and therefore subsequently in this translation (i) the IUPAC method of denoting the manner of fusion by placing the numbers and letters *after* the designation of the attached component has been adopted and (ii) the compounds are referred to as steroido[...]heterocycles when the numbering in the Russian agrees with this system (Ed. of Translation).

TABLE 1. Types of heterocyclic derivatives of steroids.

Name and formula of heterocycle	Atoms of the steroid skeleton in common with the condensed heterocycle
Five-membered heterocycles with one heteroatom	
1. Pyrrole 	1,10,9,11-, 2,3-, 3,4,5-*, 5,10,9-**, 6,5,10,19-*, 16,17-, 18,13, 17,20-*, 20,21-*
2. Indole 	2,3-, 3,4-
3. Thiophen 	4,5,6-, 5,10, 9-**
4. Selenophen 	6,5,10,19-*
Five-membered heterocycles with two heteroatoms	
5. Pyrazole 	1,2-**, 2,3-, 3,4-, 4,5-**, 15,16-, 16,17-, 16,17-**, 20,21-
6. Imidazole 	20,21-
7. Oxazole 	9,11-*, 20,21-**
8. Isoxazole 	2,3-, 2,3-**, 3,5,6-, 6,7-, 16,17,, 16, 17-**
9. Thiazole 	2,3-, 9,11-**, 11,12-, 16,17-, 20,21-, 22,23-
10. Isothiazole 	16,17-, 16, 17-**
Five-membered heterocycles with three heteroatoms	
11. Triazole 	2,3-
Six-membered heterocycles with one heteroatom	
Pyridine 	2,3-, 4,5,6-
13. Quinoline 	2,3-, 16,17-
Six-membered heterocycles with two heteroatoms	
14. Pyridazine 	2,3,4,5-**, 5,6,7,8-**
15. Pyrimidine 	2,3-, 2,3 **, 16,17-
16. Quinoxaline 	2,3-, 3,4-, 6,7-, 17,17a-, 20,21-
17. 1,3-Oxazine 	2,3-**, 3,4-**, 3,4,5-*
18. Morpholine 	3,4-**
19. 1,3-Thiazine 	1,9,10-**, 5,10,9-**
20. 1,4-Thiazine 	2,3-**
21. 1,4-Oxathiane 	2,3-**, 3,4-**
22. 1,4-Dithiane 	3,4-**
Seven-membered heterocycles*	
23. 1,2-Diazepine 	16,17-**
Condensed heterocyclic systems with several heteroatoms	
24. 1,2-Diazabicyclo-[3,2,0]heptane 	16,17-*
25. 1,9,11-Triaza-fluorene 	2,3-
26. Pteridine 	3,4-

* Fully hydrogenated heterocyclic system.
** Partly hydrogenated heterocyclic system.
*** Considered together with condensed heterocyclic systems in Section 7.

keep the same designation of the skeleton for (I) and (II), naming (II) as a derivative of 2′-methylandrostano[3,2-*c*]-pyrazole:

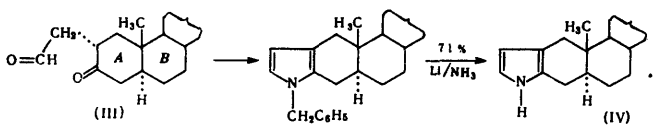


The numbering of the heterocycles adopted in the present review is shown in Table 1, in which are collected the types of heterocyclic derivatives of steroids known at present‡.

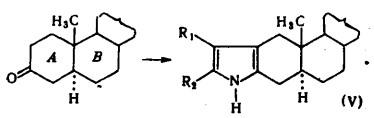
2. FIVE-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

This section deals with the steroidal derivatives of pyrrole, indole, thiophen, and selenophen.

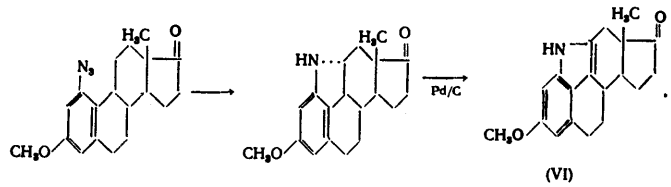
Steroids containing a pyrrole ring can be obtained by a great variety of methods. For example, three synthesis paths for steroido[3,2-*b*]pyrroles are known. The first of these consists of a Knorr cyclisation of γ-keto-aldehydes of the androstane series (III) with benzylamine; when the 1′-benzyl derivatives thus formed are reductively debenzylated, the unsubstituted androstano[3,2-*b*]pyrroles (IV) are obtained[6]:



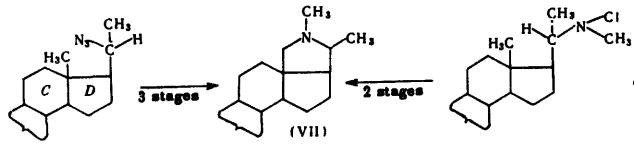
Condensation of 3-ketosteroids of the cholestane series with ethoxyiminoacetoacetate in the presence of zinc and acetic acid gives steroido[3,2-*b*]pyrroles of the type (V; $R_1 = CH_3$, $R_2 = CO_2C_2H_5$)§. Finally, in the patent literature[8] there is a description of a third method of making such compounds, by the reaction of 3-ketosteroids of the androstane series with α-aminoaldehydes or α-amino-ketones of the general formula $R_2CH(NH_2)COR_1$, where R_1 and R_2 are hydrogen or a lower alkyl radical. The reaction takes place in ethanol under the action of metallic sodium and leads to the corresponding androstano[3,2-*b*]pyrroles of type (V):



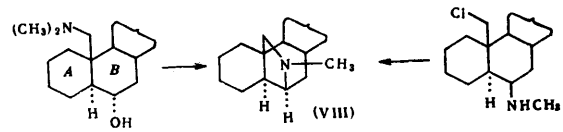
One of the methods of synthesis of partly or fully reduced pyrrolosteroids is thermal or photochemical cyclisation of azido-derivatives. Thus, the methyl ether of 1-azido-oestrone forms the 1,11α-imino-derivative on heating in n-hexadecane; the dehydrogenation of the latter leads to compound (VI), which can be considered as a derivative of pyrrole, having the atoms C_1, C_{10}, C_9, and C_{11} in common with the steroidal skeleton[9]:



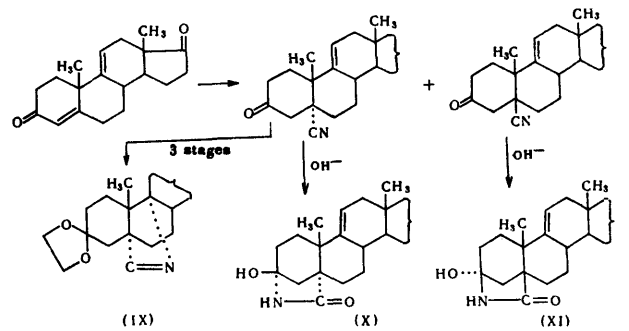
Derivatives of 1′-methylsteroidopyrrolidines (VII) can also be obtained by photolysis of 20β-azidosteroids followed by reduction with $LiAlH_4$ and *N*-methylation[10]. Another method of synthesising such compounds starts from 20α-(*N*-chloro-*N*-methylamino)steroids, which are converted into (VII) by photolysis in acid medium followed by cyclisation under the action of bases[11-14]:



Pyrrolidine derivatives of type (VIII) are also obtained by two paths — in the successive treatment of 19-dimethylamino-6α-hydroxysteroids with $CH_3C_6H_4COCl$, KI, and $LiAlH_4$ [15] and in the action of alkali on 19-chloro-6β-methylaminosteroids, which, in turn, are formed in the photolysis of 6β-*N*-chloro-*N*-methylamino-derivatives in H_2SO_4:[16]



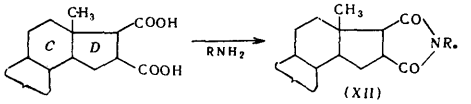
Derivatives of the steroido[3,4,5-*bc*]pyrrolidines (X) and (XI) are formed in the cyclisation by alkalis of 5α- and 5β-cyanosteroids, which are the products of the addition of HCN to Δ^4-3-ketosteroids[17,18]. When the initial steroid has $\Delta^{9(11)}$-bonds (as in the example quoted), the protection of the keto-group of the 5α-cyanosteroid by formation of the ethylene ketal, reduction of the cyano-group by $LiAlH_4$ to an imino-group, and cyclisation under the action of Al_2O_3 leads to a steroido[9,10,5-*bc*]pyrroline (IX):[17]



‡ This review does not deal with steroidal alkaloids of the conessine group, which contain a pyrrole ring, nor those of the solanidine group, which contain the quinolizine system, since their chemistry is considered in detail in corresponding monographs.[3-5]

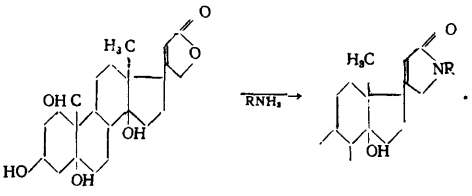
§ Derivatives of 5′-ethoxycarbonyl-4′-methylandrostano-[17,16-*b*]pyrrole were obtained in low yields from 17-ketosteroids by the same method.[7]

The cyclic imides of the 16β,17β-dicarboxysteroids (XII; R = H, alkyl, C_6H_5) are derivatives of androstano[16,17-*c*]-pyrrolidine. These compounds are active as antiepileptic agents and as depressants of the central nervous system [19]:

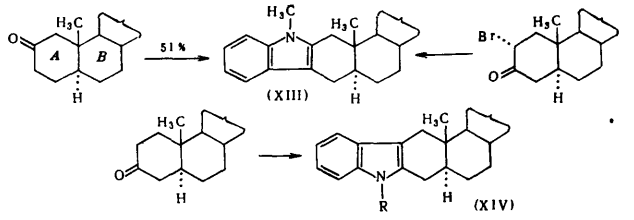


(XII)

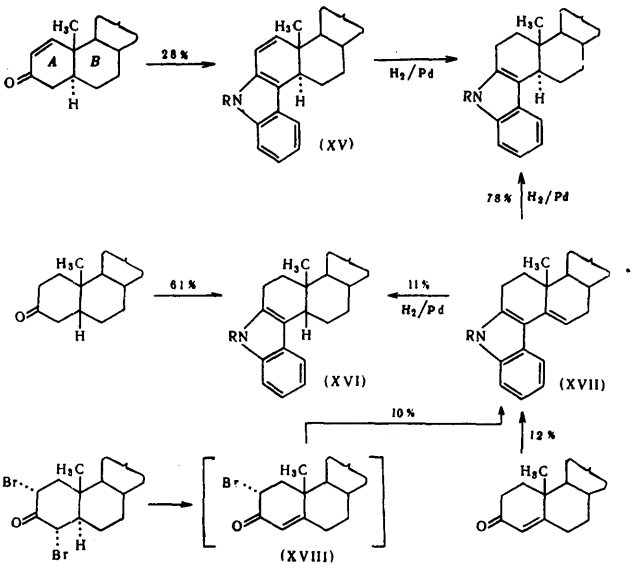
The products of the reaction of strophanthidin with primary and secondary amines can be classified among the pyrrolosteroids; these compounds not only retain the original cardiotonic activity of strophanthidin, but, unlike it, are active when introduced orally [20-22]:



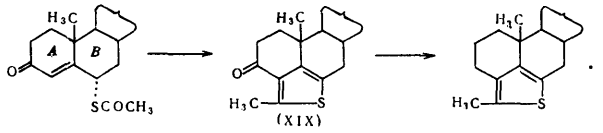
Indole derivatives condensed with the steroidal skeleton in positions 2 and 3 are formed by two methods. The first of these — a Fischer reaction with *N*-methyl-*N*-phenylhydrazine — allows 1′-methylcholestano[2,3-*b*]-indole (XIII) to be obtained from 2-ketocholestane. The same product was also obtained by the second method — by the reaction of 2α-bromocholestan-3-one with *N*-methylaniline [23]. Since the Fischer reaction usually proceeds in the direction of enolisation of the original ketones, when the 3-keto-5α-steroids of the cholestane, cholane, and androstane series react with phenylhydrazine or its *N*-methyl derivative, indolo[3,2-*b*]steroids (XIV; R = H, CH_3) are formed, isomeric to compounds of the type (XIII): [7,8,23-28]



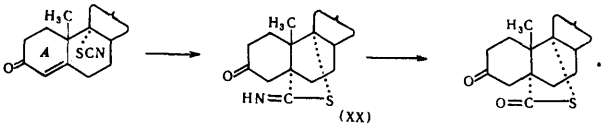
The steroido[3,4-*b*]indoles (XV)–(XVII) are formed from 3-keto-5β-cholestanes and also Δ[1]-3-keto- and Δ[4]-3-keto-cholestanes on reaction with phenylhydrazine and its α-methyl derivative (the yields shown on the scheme are for R = CH_3). [23-27] The catalytic hydrogenation of the Δ[5]-bond of the steroidoindole (XVII) leads to a mixture of the 5α- and 5β-derivatives in the ratio 7 : 1; [23] the same products are obtained by counter-synthesis from other 3-ketosteroids. Compound (XVII) is formed in low yield also on heating a mixture of 2α,4α-dibromocholestan-3-one and dimethylaniline to 200°. [28,29] The mechanism of the conversion apparently involves the reaction of the intermediate product 2α-bromo-Δ[4]-3-ketone (XVIII) with *N*-methylaniline, which is obtained *in situ* by partial demethylation of the dimethylaniline.



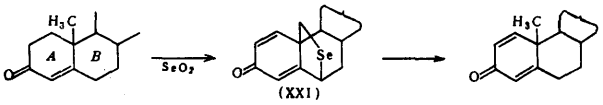
The [6,5,4-*bc*]steroid derivatives of thiophen (XIX) are formed in the chromatography of the 6α-thioacetates of Δ[4]-3-ketosteroids of the androstane, pregnane, and cholestane series on alkaline Al_2O_3. The Huang–Minlon reduction of compounds of type (XIX) give analogues without a keto-group. The thiophen derivatives of testosterone and progesterone are devoid of the usual hormonal activity [30,31]:



The imidothioethers (XX) formed in the electrolytic reduction of 9α-thiocyanatocortisol or its 17-keto-analogue, can also be considered as reduced analogues of thiophen. Hydrolysis of (XX) leads to the corresponding thiolactones [17,32]:



In the dehydrogenation of Δ[4]-3-ketosteroids by selenium dioxide, steroidal derivatives of selenophen (XXI) are formed as side-products. On treatment with Raney nickel they are converted into Δ[1,4]-3-ketosteroids [33]:



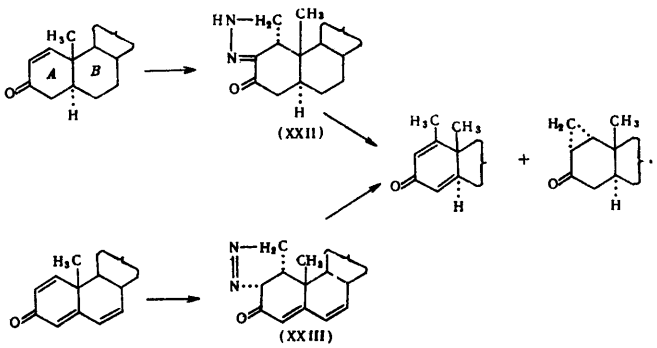
3. FIVE-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS

This group of heterocyclic derivatives of steroids includes compounds which contain pyrazole, imidazole, oxazole, isoxazole, thiazole, or isothiazole rings, and also cyclic ketals of hydroxymercapto- and dimercapto-steroids.

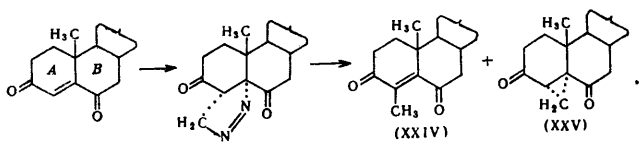
Of these compounds, the pyrazole derivatives are of the most importance practically, owing to their high physiological activity. There are two main methods used at present for the preparation of the steroidal derivatives of pyrazole. The first of these consists of the addition of a diazo-compound to the C=C double bond of unsaturated ketones and leads to steroidopyrazolines. The second method, which allows heteroaromatic steroidopyrazolines to be obtained, consists in the action of hydrazine derivatives on 1,3-dicarbonyl compounds of the steroid series.

The addition of diazoalkanes and diazoacetic ester to unsaturated steroidal ketones proceeds with a high yield (70–90%). The steroidopyrazolines obtained have no interest themselves as physiologically active compounds, but are used as intermediates in the preparation of alkylsteroids.

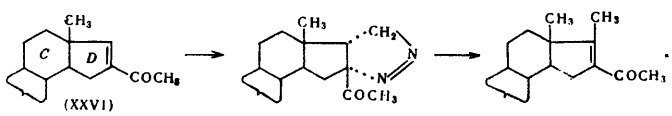
When Δ^1-3-ketosteroids of the androstane and pregnane series react with diazomethane, $\Delta^{2'}$-pyrazoline derivatives (XXII) are formed[34-39], and when $\Delta^{1,4,6}$-3-ketosteroids react, the isomeric or $\Delta^{1'}$-derivatives (XXIII).[35] Pyrolysis or acidolysis of the pyrazolines of both types leads to mixtures of the 1-methyl and 1α,2α-methylene derivatives, the ratio of which depend on the reaction conditions.



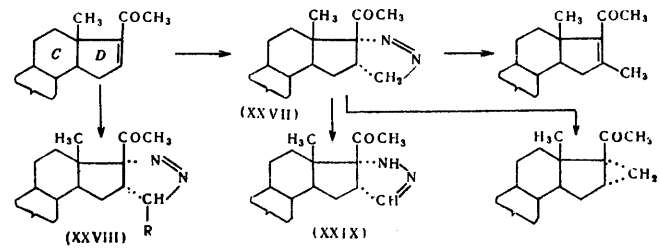
The action of diazomethane on cholest-4-en-3,6-dione leads to a pyrazoline, in the pyrolytic decomposition of which a 4-methyl derivative (XXIV) is formed, and in photolysis, a mixture of equal amounts of (XXIV) and the 4α,5α-methylene derivative (XXV):[40,41]



The 16-acetyl-Δ^{16}-steroids (XXVI) add on diazomethane at the Δ^{16}-bond, with the formation of the [17,16-*c*]pyrazoline, which forms a 17-methyl derivative on pyrolysis[42]:

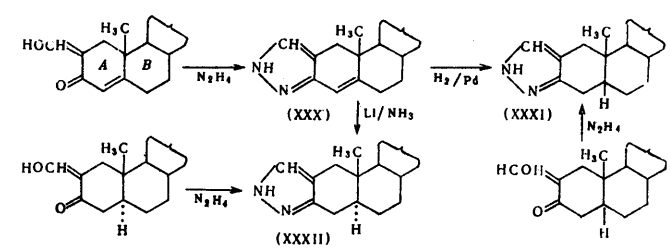


The Δ^{16}-20-ketopregnanes which are isomeric with (XXVI) react with diazomethane to form pyrazolines of the type of (XXVII), which on splitting under different conditions give mixtures of 16-methyl- and 16α,17α-methylene-steroids; the isomerisation of (XXVII) with BF_3 in dimethylformamide leads to the $\Delta^{5'}$-pyrazoline (XXIX).[35,43-51] The addition at the Δ^{16}-bond of diazoethane or diazoacetic ester with the formation of the corresponding 5'-substituted pyrazolines (XXVIII; R = CH_3, $CO_2C_2H_5$) has also been described[52,53]:

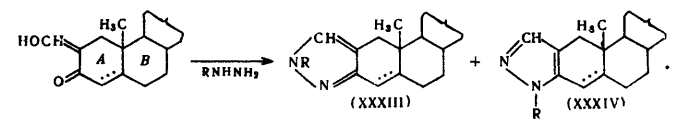


Pyrazole derivatives are usually obtained by the action of hydrazine and its analogues on hydroxymethylene or oxalyl derivatives of steroidal ketones; in individual instances cyano- and epoxy-ketones of the steroid series were also used as starting materials.

The reaction of 2-hydroxymethylene-3-ketosteroids, and also of their Δ^4- and $\Delta^{4,6}$-analogues, with hydrazine hydrate in ethanol or acetic acid leads to the formation of steroido-[3,2-*c*]pyrazoles (XXX)–(XXXII). The yields of the products usually exceed 60% and in isolated instances reach 90–95%. This method has been used to obtain pyrazole derivatives of oestrane and androstane[54-73], pregnane[61,74-81], and also cholestane and stigmastane[55,61]. Catalytic hydrogenation of the Δ^4-bond of compound (XXX) leads to 5β-dihydro-derivative (XXXI),[55,61] and Birch reduction to the 5α-isomer (XXXII);[82] in both instances the reduction does not affect the pyrazole ring.

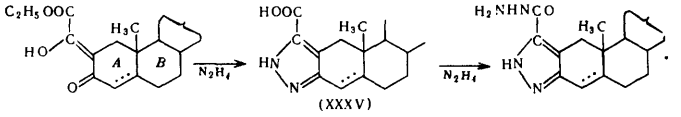


Both 1'-substituted (XXXIII) and 2'-substituted (XXXIV) steroidopyrazoles can evidently be formed when 2-hydroxymethylene-3-ketosteroids react with hydrazine homologues. Since in the alkylhydrazines the substituted nitrogen atom is more nucleophilic, when R = CH_3 the preferential formation of the isomer (XXXIII), which was also obtained in predominant amount from Δ^4-3-ketosteroids and exclusively from 3-keto-5α-steroids[2,54,57,74,83], is to be expected. With phenylhydrazine and its *p*-substituted derivatives a nitrogen atom in the β position to the phenyl group is more nucleophilic; therefore in the given instance formation of the isomer (XXXIV; R = C_6H_5) occurs preferentially or exclusively[54,74,79,84-87]:



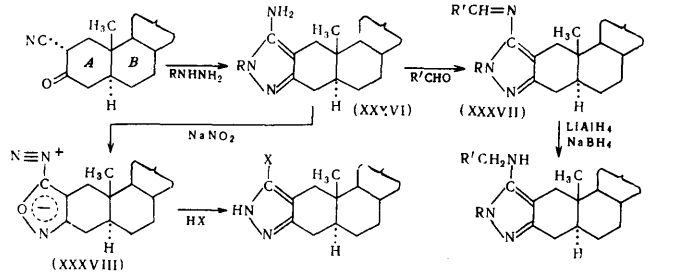
With hydrazine hydrate, 3-keto-2-oxalylsteroids form 5'-carboxypyrazoles (XXXV), the further reaction of which with hydrazine leads to the corresponding hydrazides[57,88]. In the patent literature[89] there is also a description of the

production from 3-keto-2-trifluoroacetylsteroids of the analogues (XXXV), which contain a trifluoromethyl group instead of a carboxyl group:



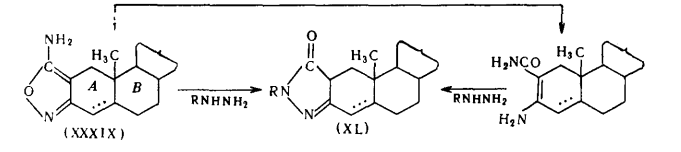
(XXXV)

On heating 2α-cyano-3-ketosteroids with hydrazine and its derivatives, 5′-aminosteroido[3,2-*c*]pyrazoles (XXXVI; R = H, CH_3, C_6H_5) were obtained. With aldehydes they form the corresponding Schiff bases (XXXVII; R′ = H, CH_3, C_2H_5, C_6H_5), the reduction of which by complex metal hydrides leads to 5′-monoamino-substituted pyrazoles. Diazotisation of 5′-aminopyrazoles (XXXVI; R = H) in aqueous medium leads to the diazopyrazoles (XXXVIII), the diazo-group of which is capable of being replaced by halogen with the formation of 5′-bromo- and 5′-iodo-derivatives [2,57]

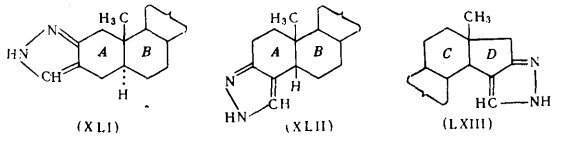


(XXXVIII)

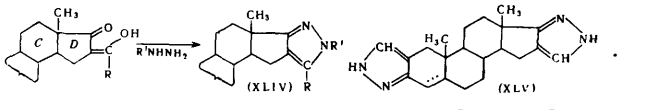
Steroidal pyrazolones of type (XL) can be obtained by two methods, by the reaction of hydrazine with 5′-aminosteroido[3,2-*c*]isoxazoles (XXXIX) or with the unsaturated β-aminocarboxamides obtained from (XXXIX) on catalytic hydrogenation [2]:



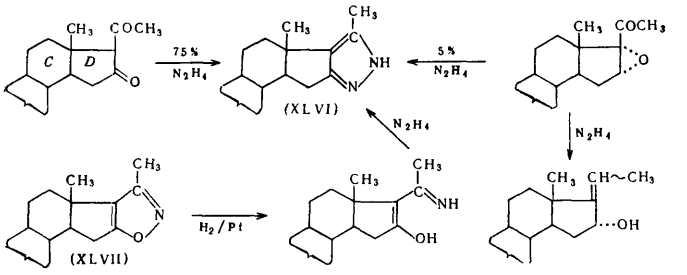
The reaction of hydrazine hydrate with 3-hydroxymethylene-2-keto- [90], 4-hydroxymethylene-3-keto- [55,61], and 15-hydroxymethylene-16-keto- [2] steroids leads respectively to steroido[2,3-*c*]- (XLI), [3,4-*c*]- (XLII), and [16,15-*c*]- (XLIII) pyrazoles:



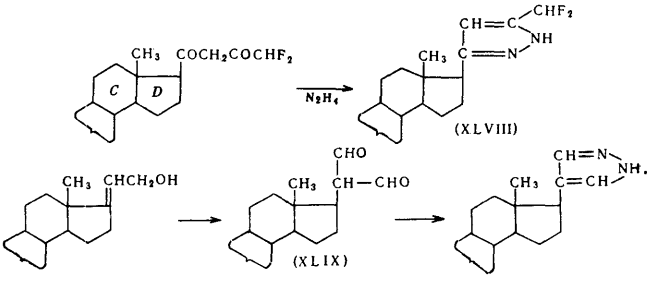
The condensation of hydrazine and its analogues with 16-hydroxymethyl- or 16-ethoxy-allyl derivatives of the 17-keto-steroids of the androstane or oestrane series leads to steroido[17,16-*c*]pyrazoles (XLIV; R = H, $CO_2C_2H_5$; R′ = H, CH_3) in 50–70% yields [91–94]. In the formation of 3,17-diketones with subsequent treatment with hydrazine, steroido[3,2-*c*:17′,16′-*c*]dipyrazoles (XLV) were obtained [2,83,95]:



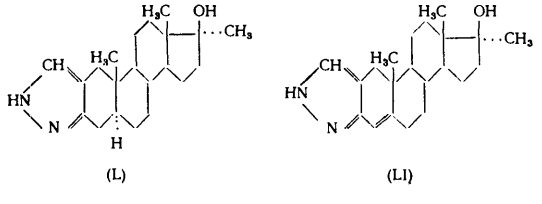
The derivatives of the 5′-methylsteroido[16,17-*c*]pyrazole (XLVI), which are isomeric with (XLIV), are formed in the reaction of 16,20-diketopregnanes with hydrazine hydrate [96–98] and as a side-product in the Huang-Minlon reduction of 16α,17α-epoxy-20-ketosteroids [99–101]; in the latter instance, the main product of the reaction is a mixture of the *cis*- and *trans*-isomers of 16α-hydroxy-$\Delta^{17(20)}$--compounds. [16,17-*c*]Pyrazoles saturated in ring A were also obtained from steroido[17,16-*d*]isoxazoles (XLVII) by the catalytic hydrogenation of the latter and reaction of the ketimines thus formed with hydrazine hydrate [102]:



Pyrazole derivatives condensed with the steroids in positions 20 and 21 were obtained by two methods. The reaction of the 21-difluoroacetyl derivative of hydroxypregnenone with hydrazine led to the 5′-difluoromethyl-[20,21-*c*]pyrazole (XLVIII). [89] The isomeric pyrazolo-[20,21-*d*] derivative is formed by the action of hydrazine on the dialdehyde (XLIX), which is obtained in six stages from $\Delta^{17(20)}$-21-hydroxysteroid [103]:



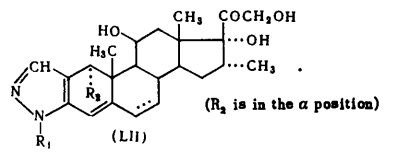
Stercido[3,2-*c*]pyrazoles of the androstane and pregnane series exhibit extremely interesting physiological activity. In the androstane series the introduction of the pyrazole grouping allows the androgenic and anabolic activities to be separated. Thus the ratio of anabolic and androgenic activities of the pyrazolo[3,2-*c*] derivatives of 4,5α-dihydro--17-methyltestosterone (L) is 120 times greater than for 17α-methyltestosterone [54]. The high value of pyrazoloandrostanes as anabolic agents is also confirmed by the results of clinical tests [34,104–110] Compounds (L) (Stanozolole, Androstanazole) and (LI) (Oxystenazole) are now manufactured on an industrial scale for use as oral anabolitics:



The introduction of electron-withdrawing substituents (CO_2H, $CONHNH_2$) into the 5′ position of the pyrazole ring

lowers the anabolic activity in comparison with the unsubstituted compounds and with analogues with 5′ electron--donating substituents (CH_3, NH_2).[2] With the unsaturated Δ^4- and $\Delta^{4,6}$-derivatives, with a fall in the anabolic activity the appearance of significant oestrogenic activity was noted[54,60,111]. The introduction of 6α-CH_3, 7α-$SCOCH_3$, or 9α-F-11β-OH groupings into the steroidal nucleus of pyrazoloandrostanes sharply reduces the anabolic activity, which is the exact opposite to the unsubstituted androstanes, in which such substitution increases the activity[54,62].

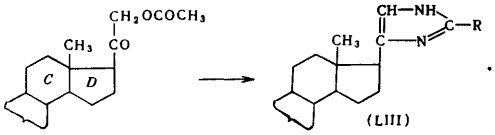
Derivatives of corticosteroids with [3,2-*c*]pyrazole rings with 2′-aryl substituents (LII) are the most active of the known anti-inflammatory agents, hundreds and even thousands of times more active than cortisol (Table 2). The activity is increased on the introduction of *p*-fluoro-substituent into the 2′-phenyl nucleus and reduced by the introduction of any other substituent. The isomeric 1′-phenylpyrazoles are of low activity. It is very important that the increase in anti-inflammatory activity on the introduction of the pyrazole ring is not accompanied by an increase in the mineralocorticoidal activity[74,84-86,112].



(LII)

Unlike the steroido[3,2-*c*]pyrazoles, the derivatives of oestrane and androstane (XLIV) and (XLVI) with pyrazole rings in positions 16 and 17 are almost completely devoid of oestrogenic and androgenic activity. At the same time these derivatives retain the hypocholesterolemic and, to some extent, the anabolic activity of the original compounds[91-93,97].

The [20,21-*d*] derivatives of imidazole (LIII) were obtained by the reaction of 21-acetoxy-20-ketopregnanes with $Cu(OCOCH_3)_2$, NH_3, and CH_2O in ethanol, with subsequent decomposition of the copper salt formed by hydrogen sulphide. Use of acetaldehyde or benzaldehyde instead of formaldehyde allows the corresponding 2′-substituted imidazoles (LIII; R = CH_3, C_6H_5) to be obtained[113]. It has been shown[114] that these compounds reduce the blood pressure. The hypotensive activity decreases on alkylation of the imidazole ring and the introduction of oxygen substituents in position 11:

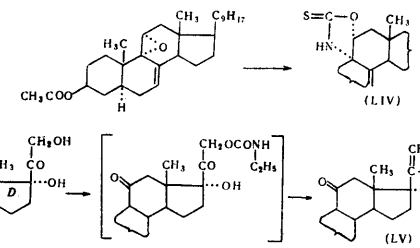


(LIII)

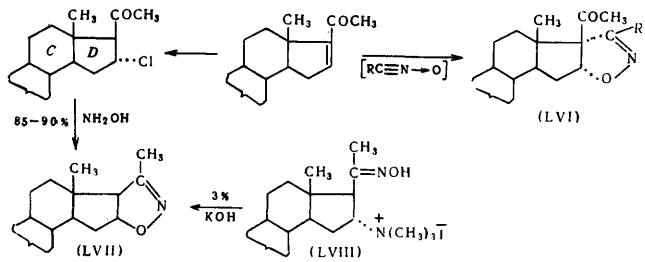
TABLE 2. Anti-inflammatory activity of steroido[3,2-*c*]pyrazoles of type (LII) in a test on the suppression of granuloma.[74,84-86,112]

Substituent			Anti-inflammatory activity (control = 1)
R_1	R_2	presence (+) or absence (−) of Δ^1-bond	
H	F	−	10
p-ClC_6H_4	H	−	15
C_6H_5	H	−	60
p-FC_6H_4	H	−	100
2,4-$F_2C_6H_4$	H	+	115
p-FC_6H_4	F	−	500
p-FC_6H_4	H	+	600
C_6H_5	F	+	2000

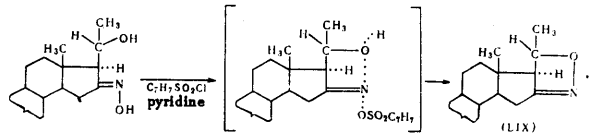
Steroidal derivatives containing a partly or completely hydrogenated oxazole ring have as yet been obtained in only two instances. The action of thiocyanic acid in ether on 9α,11α-epoxide of the ergostane series leads to a [9,11-*d*] derivative of oxazolidine (LIV); its formation apparently includes the anomalous *cis*-9α,11α-opening of the epoxide ring[115]. In the reaction of prednisone with ethyl isocyanate, instead of the expected 21-carbamate a product of its cyclisation was obtained, the [20,21-*d*]oxazolidone (LV):[116]



Derivatives of isoxazole have been studied much more. Three methods of synthesis are known for partly reduced derivatives. 3′-Methylandrostano[17,16-*d*]isoxazolines (LVII) are formed in high yield in the formation of oximes of 3β-acetoxy-16α-chloropregnenone and with low yield in the treatment of the trimethylammonium iodide derivative (LVIII) with alkali[117]. The reaction of Δ^{16}-20--ketopregnanes with nitryl oxides formed *in situ* by the treatment of the hydrochlorides of hydroxamic acids with triethylamine, gave, as a result of 1,3-dipolar addition, pregnano[17,16-*d*]isoxazolines (LVI; R = CH_3, C_6H_5) in 50–95% yields[118]:

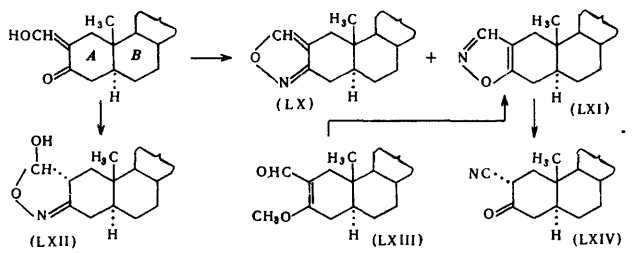


Under Beckmann rearrangement conditions, the oximes of 16-keto-20α-hydroxysteroids yield 5′-methylandrostano-[16,17-*c*]isoxazolines (LIX). The most probable mechanism is cyclisation from the anti-forms of the initial oxime with retention of the $C_{(20)}$ configuration[119]:

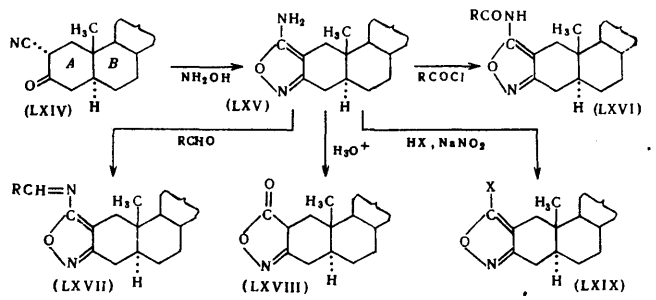


The principal starting materials for obtaining heteroaromatic isoxazolosteroids are the oxymethylene-, cyano-, and epoxy-ketones of the steroid series. Reaction of 2-hydroxymethylene-3-ketosteroids with hydroxylamine leads to a mixture of steroido[3,2-*c*] (LX) and [2,3-*d*] (LXI) isoxazoles[57-59,120-128]. When the reaction is carried out under mild conditions, in addition to these products up to 15% of 5′-hydroxy[3,2-*c*]-2′-isoxazolines (LXII) are formed, which are converted into (LX) on heating with acetic anhydride[124,129]. The ratio of (LX) to (LXI) depends on the pH, the solvent, and temperature. Thus when it is carried out in aqueous alcohol, 8% (LX) and 82% (LXI) are obtained, but in pyridine solution the composition of the

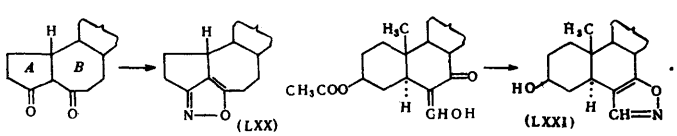
mixture is the reverse — 91% (LX) and 6% (LXI).[123,124] The reaction of Δ^4-, $\Delta^{4,6}$-, and 4,4-dimethylsteroids leads exclusively to [2,3-*d*]isoxazoles (LXI).[58,120,122,124] The same products are also formed from methoxy-derivatives of type (LXIII).[72] On treating the reaction products with sodium methoxide the [3,2-*c*] derivatives (LX) remain unchanged, but the [2,3-*d*] derivatives are converted into 2α-cyano-3-ketosteroids (LXIV).[57,122-125] This reaction allows mixtures of (LX) and (LXI) to be separated, and also serves as a convenient preparative method for the synthesis of 2α-cyanosteroids (LXIV):



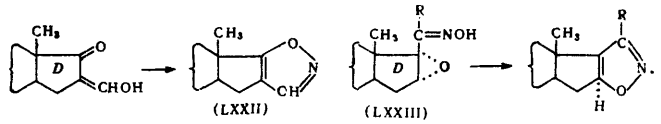
In an analogous manner to the above synthesis of 5'-aminopyrazoles, the reaction of (LXIV) with $NH_2OH.HCl$ in pyridine leads to 5'-amino[3,2-*c*]isoxazoles (LXV).[57] The 5'-amino-group of compound (LXV) is easily acylated by acyl chlorides and by ethyl chlorocarbonate with the formation of the corresponding acylates (LXVI; R = alkyl) and urethanes (LXIV; R = OC_2H_5).[2] Condensation with aldehydes gives Schiff bases (LXVII), which are reduced by sodium tetrahydroborate to the corresponding 5'-alkylamino-derivatives. On hydrolysis of (LXV) with mineral acids, deamination occurs with formation of the 5'-isoxazolones (LXVIII) but diazotisation in HCl or HBr allows the corresponding halo-derivatives to be obtained (LXIX).[2] The derivatives of 5'-aminoisoxazole are used as intermediates for the synthesis of other heterocycles — mainly analogues of pyrazole and pyrimidine.



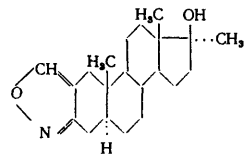
The 3,6-diketo-derivatives of A-nor-B-homo-oestrane react with hydroxylamine to form [3,5,6-*cd*]isoxazoles (LXX) which exhibit anabolic activity[130,131]. Under the same conditions 6-hydroxymethylene-7-ketocholestanol gave a [6,7-*d*]isoxazole derivative (LXXI):[120]



The action of hydroxylamine on 16-hydroxymethylene--17-ketosteroids of the androstane and oestrane allows [16,17-*d*]isoxazoles (LXXII) to be obtained[132]. Their isomers, the [17,16-*d*]isoxazoles, are formed in the dehydration of oximes of the (LXXIII; R = CH_3, C_6H_5) type with $POCl_3$ in pyridine[133]:

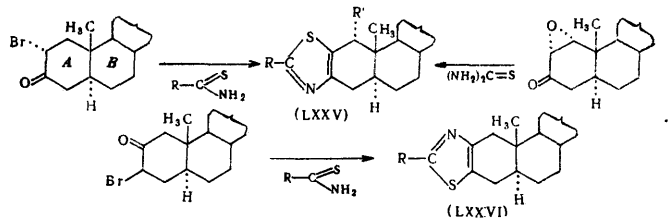


The introduction of the isoxazole grouping in the 2,3-position of androstane leads to an increase in the anabolic and a reduction in the androgenic activity. The [2,3-*d*] isomers are the more active in this. The introduction of Δ^4- and Δ^6-bonds, and also of 3'-alkyl, 4,4-dimethyl, and 6α-methyl substituents lowers both forms of activity[34,124]. Results have been obtained[58,120] on the presence of antitumour activity in the Δ^4-androstano[2,3-*d*]isoxazoles. Unlike the pyrazolosteroids, the isoxazolo[2,3-*d*] derivatives of the corticosteroids are devoid of hormonal activity[122]. Compound (LXXIV) has found practical application as an anabolic agent under the name of "Androisoxazole"[134-138]:

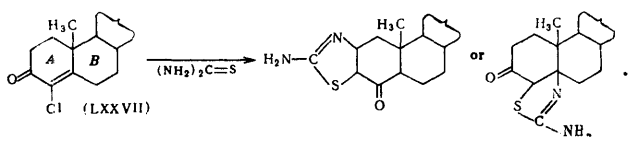


(LXXIV)

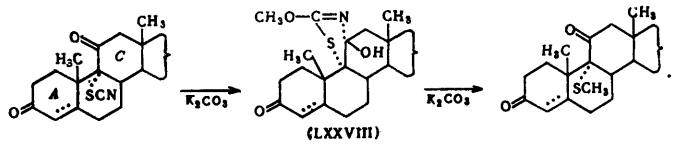
The [3,2-*d*] derivatives of thiazole are formed on boiling alcoholic solutions of 2α-bromo-3-ketosteroids of the androstane, pregnane, and cholestane series with thiourea and its *N*-alkyl derivatives[7,139-143], and also with thioamides[122,140,144-146]. In the first instance 2'-alkylaminothiazolosteroids (LXXV; R = NH_2, $NHCH_2CH{=}CH_2$, NHC_6H_5; R' = H) were obtained in 30–80% yields and in the second 2'-alkylthiazolosteroids (LXXV; R = H, CH_3; R' = = H) in 20–50% yields. 1α-Hydroxy-derivatives (LXXV; R = NR_2; R' = OH) are formed by the action of thiourea on 1α,2α-epoxy-3-ketopregnanes[147]. Reaction of 3β-bromo--2-ketosteroids with thioamides gave the isomeric (LXXV) [2,3-*d*]thiazole derivatives (LXXVI; R = H, CH_3, C_6H_5).[148] High anabolic and low androgenic activity has been noted for both types of derivative in the androstane series[145,148], and in the pregnane series there is anti-inflammatory activity[147].



Androstane derivatives of 2'-aminothiazole were also obtained in the treatment of 4-chloro-Δ^4-3-ketosteroids (LXXVII) with thiourea in alkaline medium; but it was not shown whether the compounds possessed [2,3-*d*] or [4,5-*d*] structures[139]:

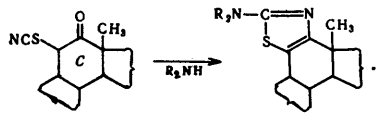


The 9α-thiocyano-derivatives of adrenosterone and cortisone are converted into 2′-methoxysteroido[11,9-*d*]thiazolines (LXXVIII) in 50–70% yields by the action of a solution of potassium carbonate in aqueous methanol at room temperature. Boiling with potassium carbonate solution allows (LXXVIII) to be converted into the 9α-methylthio-derivatives in 35–50% yields. When there are Δ^1- or Δ^4-bonds in the molecule, boiling a solution of (LXXVIII) in methanol leads to isomerisation into thiazine derivatives (see below)[149,150]:



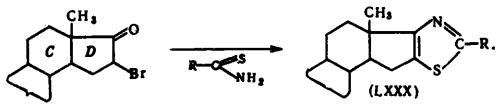
(LXXVIII)

The reaction of 12-keto-11β-thiocyanosteroids of the cholane and spirostane series with secondary amines in dioxan leads to 2′-piperidinosteroido[12,11-*d*]thiazoles (LXXIX) or the corresponding 2′-morpholino-, 2′-piperazino-, and 2′-diethylamino-derivatives. The compounds obtained exhibit antihormonal activity[151,152]:



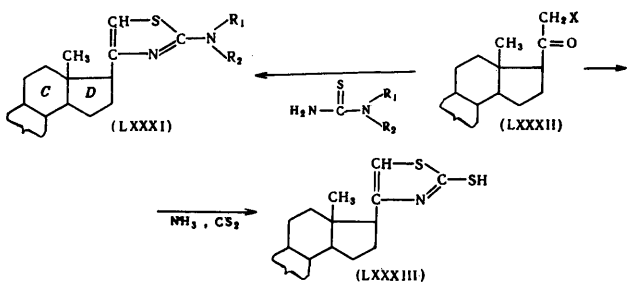
(LXXIX)

On heating 16β-bromo-17-ketosteroids with thioacetamide or thiourea in ethanol, 2′-substituted [17,16-*d*]thiazole derivatives (LXXX; R = CH_3, NH_2) are obtained[153,154]:



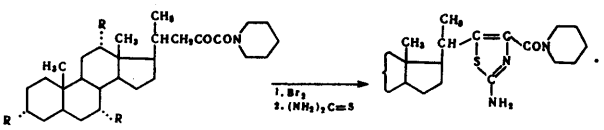
(LXXX)

2′-Aminosteroido[20,21-*d*]thiazoles (LXXXI) are formed in the condensation of thiourea and its *N*-alkyl derivatives with 21-substituted 20-ketopregnanes (LXXXII; X = Cl, I, OH, OSO_2CH_3, $OSO_2C_6H_4CH_3$). When X = I the yields reach 80–100%, but when X = $OSO_2C_6H_4CH_3$ they do not exceed 35–60%.[155-160] The reaction of (LXXXII; X = Cl) with ammonia and carbon disulphide in ethanol leads to a 2′-mercapto-derivative (LXXXIII).[161] The products obtained are cardiotonic media with a toxicity lower than for the heart aglycones[155,126].

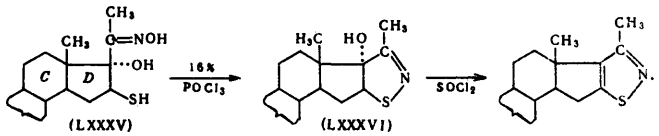


(LXXXI) (LXXXII) (LXXXIII)

The last group of thiazolosteroids — [23,22-*d*]thiazole derivatives — was obtained on successive bromination and treatment with thiourea of the piperidylamides of 23-ketocholanic acids (LXXXIV; R = H, $OCOCH_3$):[162]

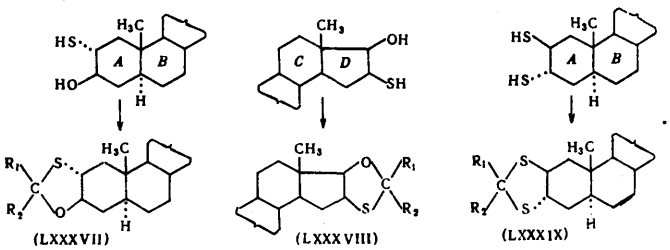


The Beckmann rearrangement of the oxime (LXXXV) under the action of $POCl_3$ in pyridine gives compound (LXXXVI), dehydration of which leads to a derivative of androstano[17,16-*d*]isothiazole[153,163,164]. This reaction is still the sole example of the synthesis of steroid derivatives of isothiazole:



(LXXXV) (LXXXVI)

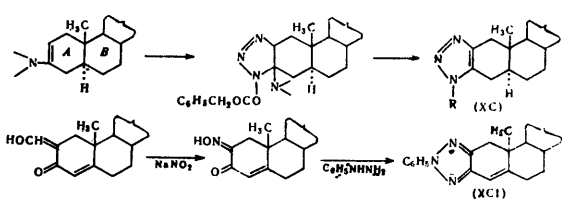
In this section mention must also be made of the preparation of heterocyclic derivatives of the androstane and cholestane series (LXXXVII)–(LXXXIX) by the reaction of vicinal hydroxymercapto- and dimercapto-steroids with aldehydes and ketones[165-169]:



(LXXXVII) (LXXXVIII) (LXXXIX)

4. FIVE-MEMBERED HETEROCYCLES WITH THREE HETEROATOMS

Derivatives of triazole condensed with ring A of the steroidal system have been synthesised by two methods. According to the first of these, enamines of the 3-keto-5α-steroids of the androstane and pregnane series are reacted with benzyl azidoformate, to form 1′-benzyloxycarbonylsteroido[2,3-*d*]triazoles, the hydrogenolysis of which by lithium tetrahydroaluminate leads to unsubstituted [2,3-*d*]-triazoles (XC; R = H).[170,171] The compounds of the type (XC; R = C_6H_5) can also be obtained directly from the enamines by reaction with phenyl azide[170-172]. The second method of synthesis starts from hydroxymethylene derivatives of Δ^4-3-ketopregnanes, which on treatment with $NaNO_2$ and the subsequent reaction of the keto-oximes obtained with phenylhydrazine gives 2′-phenylsteroido[2,3-*d*]triazoles (XCI):[172]

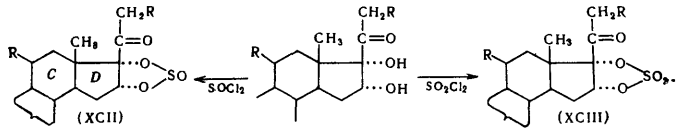


(XC) (XCI)

The introduction of the 1′-phenyl[2,3-*d*]triazole grouping in the molecule of corticosteroids raises by a factor of 5–7

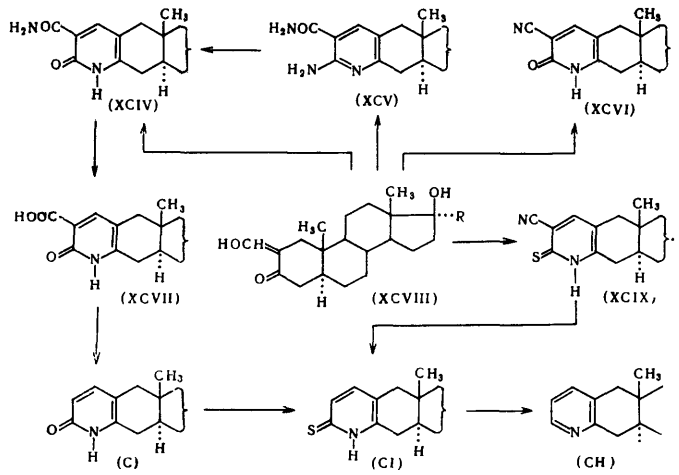
the anti-inflammatory activity of the latter. On the other hand, isomeric 2′-phenyltriazoles (XCI) are devoid of anti-inflammatory activity, which shows its high structural specificity [172].

The cyclic sulphites (XCII) and sulphates (XCIII) of 16α,17α-dihydroxysteroids can also be included among the five-membered heterocycles with three heteroatoms. Compounds of this type with R = H have a high gestagenic activity, and those with R = OH have anti-inflammatory activity [173-176]:

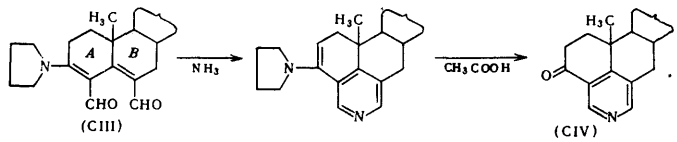


5. SIX-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

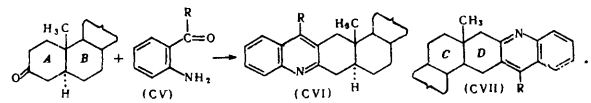
Derivatives of pyridine and quinoline belong to this group of heterocyclic steroids. Androstano[3,2-*b*]pyridines are formed by the reaction of 2-hydroxymethylene-3-keto-steroids (XCVIII; R = H, CH_3) with cyanoacetamide and its derivatives. On boiling a mixture of the reagents in ethanol with triethylamine leads to a cyanopyridone (XCVI) and when the reaction is carried out at 180° without a solvent the carboxamide (XCIV) is obtained. Compound (XCVI) is also formed in low yield on boiling (XCVIII) with malononitrile. The reaction of (XCVIII) with cyanothioacetamide gives the cyanothiopyridone (XCIX) in good yield, and that with malonamide amidine gives the 6′-amino-derivative (XCV), the diazotisation of which leads to (XCIV). Alkaline hydrolysis of (XCIV) gives a pyridone carboxylic acid (XCVII), which at 300° is decarboxylated into the pyridone (C). The thiopyridone (CI) was obtained in analogous fashion; it is also formed from (C) by the action of P_2S_5 in pyridine. The reductive desulphidation of (CI) by Raney nickel gives the androstano[3,2-*b*]pyridine (CII). This compound has a high ratio of anabolic to androgenic activity, but both types of activity are weak [177-179]:



The dialdehyde (CIII), obtained from the pyrrolidylenamine of testosterone by the Vilsmeyer reaction (dimethylformamide and $POCl_3$), under the action of gaseous ammonia in methanol solution gives enamines, the hydrolysis of which by acetic acid leads to a derivative of androstano[4,5,6-*cd*]-pyridine (CIV): [180]



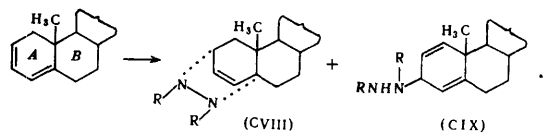
The condensation of 3-keto-derivatives of cholane and cholestane with *o*-aminobenzaldehyde (CV; R = H), anthranilic acid (CV; R = OH), and isatin (CV; R = CO_2H) gives the corresponding 4′-substituted steroido[3,2-*b*]quinolines (CVI). Decarboxylation of (CVI; R = CO_2H) by heating in a vacuum allows the 4′-unsubstituted analogues [7,181-183] to be obtained. Steroido[17,16-*b*]quinolines (CVII; R = H, CO_2H) were obtained in a completely analogous fashion from 17-keto-derivatives of androstane and oestrane in yields of up to 90%. [182,183] It is reported [182] that compounds of the type of (CVI) and (CVII) exhibit haemolytic activity:



6. SIX-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS

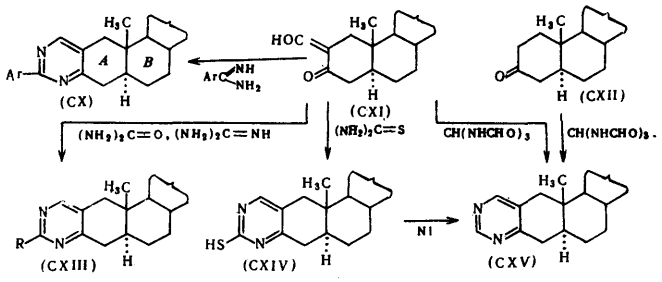
This section deals with the steroidal derivatives of pyridazine, pyrimidine, quinoxaline, 1,3-oxazine, morpholine, 1,3- and 1,4-thiazine, 1,4-oxathiane, and 1,4-dithiane.

A diene condensation of cholesta-2,4-diene with diethyl azoformate on boiling in benzene leads to a mixture of 21% of a cholestano[2,3,4,5-*cde*]tetrahydropyridazine (CVIII; R = $CO_2C_2H_5$) derivative and 11% of a substitutional addition product (CIX; R = $CO_2C_2H_5$). For cholesta-5,7-diene the yield of pyridazino-derivative drops to 4%, and in the mixture the substituting addition product is greatly predominant (yield 36%): [184]

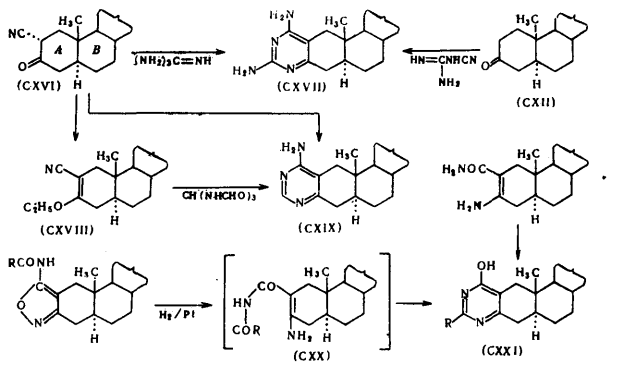


One of the methods of synthesising steroido[3,2-*d*] derivatives of pyrimidine is the reaction of 2-hydroxymethylene-3-ketosteroids (CXI) with various amino-compounds. With the hydrochlorides of arylamidines (acetamidine does not react) (CXI) forms 2′-aryl derivatives (CX; Ar = phenyl, *o*- and *p*-nitrophenyl, pyridyl) [122,145,185-187], with urea and thiourea, 2′-hydroxy- (CXIII; R = OH) and 2′-mercapto-derivatives (CXIV), [57] and with guanidine, the 2′-amino-derivative (CXIII; R = OH_2). [57,188] Treatment of (CXI) or the unsubstituted 3-ketosteroids (CXII) with

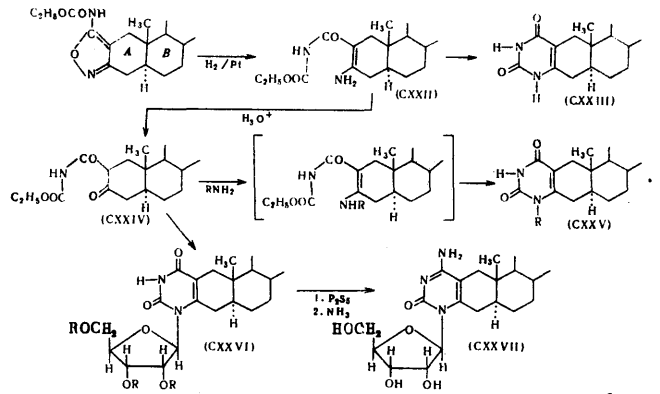
trisformylaminomethane gives 2′-unsubstituted [3,2-*d*]-pyrimidines (CXV), which are also formed in the reduction by Raney nickel of 2′-mercapto-derivatives (CXIV):[57]



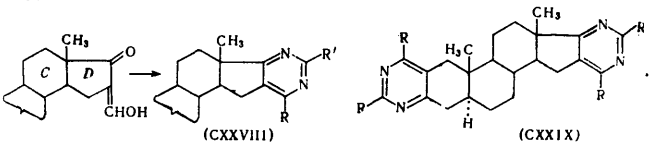
Another group of pyrimidine derivatives with substituents in the 6′-position was obtained from 2α-cyano-3-keto-steroids (CXVI) and their enol ethers (CXVIII). Reaction with trisformylaminomethane led to the 6′-amino-derivative (CXIX) and reaction with guanidine to the 2′,6′-diamino-derivative (CXVII). The last group of compounds is formed also on fusing (200–250°) 3-ketosteroids (CXII) with cyanoguanidine[2,189]. The β-aminocarboxamides obtained from 5′-aminoisoxazoles (see Section 3) react with amidines or trisformylaminomethane to form 6′-hydroxy[3,2-*d*]pyrimidines (CXXI) containing hydrogen, alkyl, or aryl in the 2′ position. The same compounds were obtained from 5′-acylaminoisoxazoles, the catalytic hydrogenation of which gives *N*-acyl derivatives (CXX), which are cyclised in the course of the reaction into (CXXI; R = alkyl, aryl)[2]:



2′,6′-Dihydroxypyrimidines tautomeric with the 2′,6′-diketotetrahydropyrimidines were obtained from 5′-ethylurethanoisoxazoles (see Section 3). Catalytic hydrogenation gave the 2-(*N*-ethoxycarbonyl)carboxamide (CXXII), which is readily cyclised into 2′,6′-diketo-derivative (CXXIII). On the other hand, acid hydrolysis of (CXXII) leads to the corresponding 3-ketone (CXXIV), which reacts with primary amines to form enamines which are cyclised into derivatives of 3′-alkyl-2′,6′-diketoandrostano[3,2-*d*]-pyrimidine (CXXV; R = alkyl, cycloalkyl, aryl). By using 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosylamine as the primary amine, a steroidal nucleoside was obtained — a derivative of uridine (CXXVI; R = H). Treatment of the tribenzoyl derivative (CXXVI; R = $OCOC_6H_5$) with phosphorus pentasulphide in pyridine and subsequent amination led to a steroidal analogue of cytidine (CXXVII):[2]

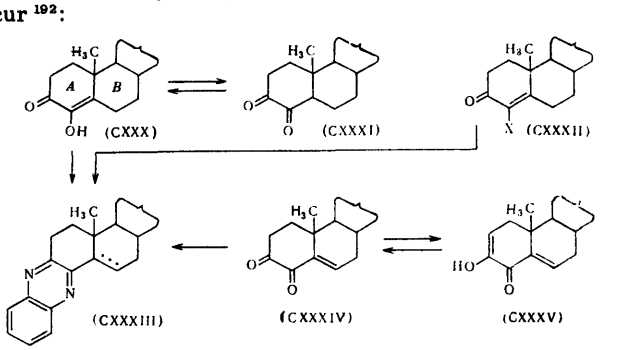


The reaction of 16-hydroxymethylene-17-ketosteroids with trisformylaminomethane, acetamidine, or cyanoguanidine gave the corresponding [17,16-*d*]pyrimidines (CXXVIII; R = H, NH_2; R′ = H, CH_3). [3,2-*d*:17,16-*d*]-Dipyrimidines (CXXIX; R = H, NH_2) were obtained from 2,16-bishydroxymethylene-3,17-diketosteroids by the same methods[2,95,189–191]:



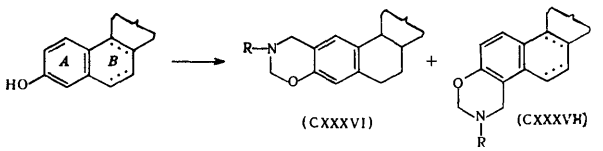
Both [3,2-*d*] and [17,16-*d*]pyrimidine derivatives of androgenic and oestrogenic hormones almost completely loss the hormonal activity and are completely devoid of anabolic and anticholesterolemic activity. Moreover they exhibit significant antibacterial activity against Gram-positive micro-organisms[2,189].

The formation of quinoxaline derivatives of steroids on reaction with *o*-phenylenediamine serves as a proof of the existence of α-diketo-groupings in the molecule. Examination of the conditions of formation of these derivatives is most convenient with the 3,4-diketones. Saturated diketones exist predominantly in the ketoenol form (CXXX), not in the diketo-form (CXXXI), and react with phenylenediamine only on fusion up to 120°.[192] The same product — the [3,4-*b*]quinoxaline (CXXXIII) — is formed also on boiling the 4-bromo- and 4-chloro-derivatives (CXXXII; X = = Br, Cl) with *o*-phenylenediamine in acetic acid[193,194]. The diketone (CXXXIV) and ketoenol (CXXXV), which contain the Δ^5 bond, give the same quinoxaline derivative but (CXXXIV) reacts when a solution of the components in ethanol is heated, whereas (CXXXV) requires fusion of a mixture of the dry components at 135° for reaction to occur[192]:

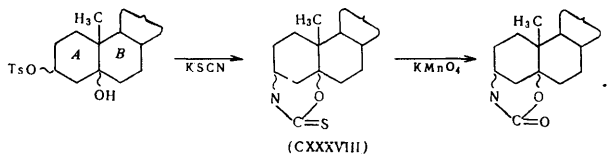


The preparation of quinoxaline derivatives from 2,3-diketo-[195], 6,7-diketo-[196], and 20,21-diketo-[197-199] steroids and also from 17,17a-diketones of the D-homo series[200] has been described.

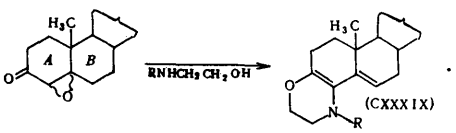
The reaction of phenolosteroids with formaldehyde and amines in the presence of alkali leads to the production of 1,3-oxazines. When only ring A is aromatic, then mixtures (in 30–50% yields) of steroido[2,3-*e*] (CXXXVI) and [3,4-*e*] (CXXXVII) oxazines in the ratios from 3 : 1 to 6 : 1 are formed (R = cyclohexyl, benzyl, phenethyl). Compounds with aromatic rings A and B are converted with yields of ~ 80% into homogeneous [3,4-*e*] analogues. The products obtained exhibit significant antitumour activity[201,202]:



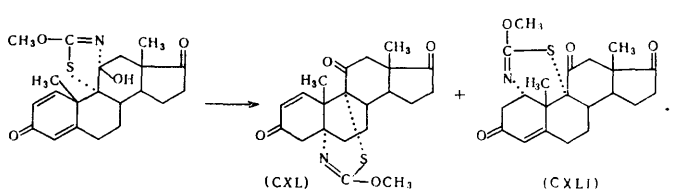
The tosylates of the epimeric 3β,5α- and 3α,5β-dihydroxycholestanes react with potassium thiocyanate to form [4,5,6-*de*] derivatives of 1,3-perhydro-oxazinethione (CXXXVIII) with the 3α,5α- and 3β,5β-configurations respectively. Permanganate oxidation converts (CXXXVIII) into the corresponding perhydro-oxazinones[203]:



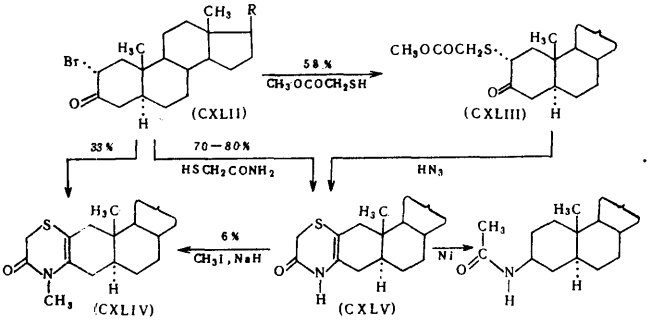
The 4′-alkyl[3,4-*b*]morpholines (CXXXIX) were obtained by boiling in ethylene glycol a mixture of 4,5-epoxy-17α-methyltestosterone and *N*-alkylaminoethanols[204]:



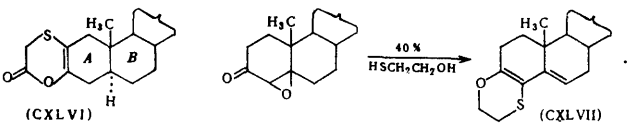
Derivatives of 1,3-thiazine are formed on boiling in methanol the androstano- and pregnano-[11,9-*d*]thiazolines and with a Δ^1 or Δ^4 bond, described in Section 3. The isomerisation involves breaking of the C–N bond at $C_{(11)}$ and the attachment of nitrogen to $C_{(1)}$ or $C_{(5)}$; as a result the Δ^4 compounds give the [5,10,9-*de*]-1,3-thiazine derivatives (CXL), and the Δ^1 compounds the [9,10,1-*de*]-1,3-thiazine derivatives (CXLI). When there is the $\Delta^{1,4}$-3-keto-structure the Δ^1 bond reacts preferentially; thus, in the example shown below the ratio of the products with cyclisation at the Δ^4 and Δ^1 bonds is (CXL) : (CXLI) = 1 : 7.[149,150]:



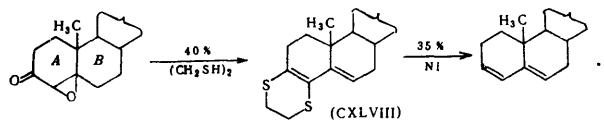
Condensation of 2α-bromo-3-ketosteroids (CXLII) of the androstane (R = $OCOCH_3$) or pregnane (R = $COCH_3$) series with mercaptoacetamide in collidine leads to high yields of [3,2-*e*] derivatives of 1,4-thiazenones (CXLV). The formation of 3-acetamido-derivatives in the desulphurisation of (CXLV) confirms that nitrogen is joined to the $C_{(3)}$ atom of the steroidal skeleton. *N*-Methylation of (CXLV) gives, in low yields, the 4′-methyl derivatives (CXLIV) which can be obtained more conveniently from (CXLII) by reaction with *N*-methylmercaptoacetamide. Another method of making (CXLV) consists in the condensation of (CXLII) with methylmercaptoacetate followed by treatment of the mercapto-derivative formed (CXLIII) with ammonia. Thiazenones of the androstane series have a ratio of anabolic to androgenic activity of 4–8 (methyltestosterone = 1):[205,206]



The cyclisation of the mercapto-derivative (CXLIII) under the action of *p*-toluenesulphonic acid in benzene gave the [2,3-*e*] derivative of 1,4-oxathiane (CXLVI) in 54% yield[205,206]. Steroido[3,4-*b*]-1,4-oxathianes (CXLVII) were obtained in the reaction of 4β,5β-epoxy-3-ketones of the androstane and cholestane series with mercaptoethanol under the action of polyphosphoric acid[207]:



In an analogous fashion to the formation of (CXLVII), 4β,5β-epoxycholestan-3-one with ethanedithione gives $\Delta^{3,5}$-cholestadieno[3,4-*b*]-1,4-dithiane (CXLVIII), the reductive desulphurisation of which by Raney nickel leads to $\Delta^{3,5}$-cholestadiene[207]:

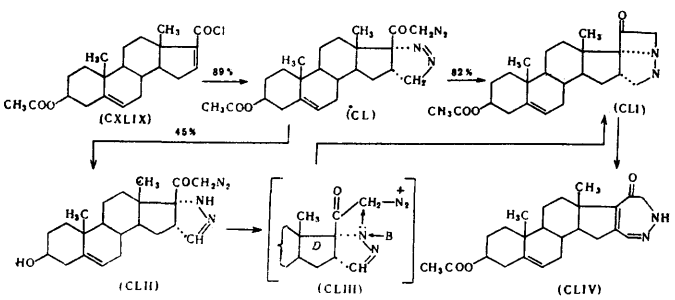


7. CONDENSED HETEROCYCLIC SYSTEMS WITH SEVERAL HETEROATOMS

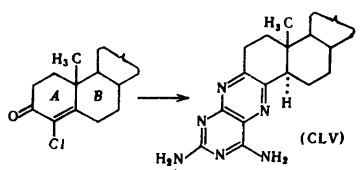
Steroidal derivatives of 1,2-diazabicyclo[3,2,0]-heptane are formed by the reaction of two molecules of diazomethane with 3β-acetoxy-5,16-etiadienyl chloride (CXLIX). The 21-diazo[17,16-*c*]pyrazoline (CL) obtained in the first stage loses nitrogen when heated with acetic acid and (CLI) 16α,17α,21-[3,1,1-(2-pyrazolino)]-5-pregnen-3β-ol-20-one acetate¶ is formed. Alkaline hydrolysis of the acetate (CL) is accompanied by migration of the

¶ Better named 3′-oxoazetidino[1′,2′ : 2,3]pyrazolidino[4,3-*k*]-androst-5-en-3-yl acetate (Ed. of Translation).

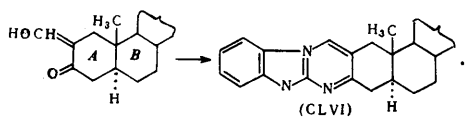
double bond in the pyrazoline ring from the $\Delta^{1'}$- to the $\Delta^{2'}$--position. Since the compound obtained (CLII) is cyclised into (CLI) more readily than the $\Delta^{1'}$-isomer (CL) the sequence of reactions (CL) → (CLII) → (CLI) was adopted. The most probable mechanism of the cyclisation is the attack of the nitrogen of the pyrazoline ring by the protonated diazoketone (CLIII). On heating (CLI) with a mixture of acetic acid and sodium acetate there is rupture of the bond between $C_{(17)}$ and nitrogen with the formation of a [17,16-*d*]diazepinone (CLIV), which are the sole representatives of steroidal derivatives with seven-membered heterocycles[208-210]:



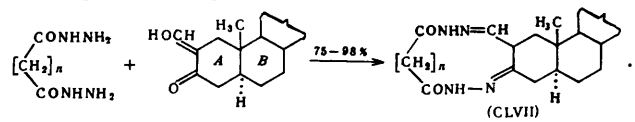
The reaction of 4-chlorotestosterone acetate with an excess of 2,4,5,6-tetra-aminopyrimidinium hydrogen sulphate in a mixture of ethanol and acetic acid gives a derivative of 2',4'-diaminoandrostano[4,3-*g*]pteridine (CLV), which is a highly active antagonist for folic acid[211]:



A third representative of condensed heterocycles — cholestano[3,2-*b*]-1',9',11'-triazafluorene (CLVI) — was obtained in good yield by the reaction of 2-hydroxymethylenecholestan-3-one with 2-aminobenzimidazole[7]:



In conclusion, mention must be made also of the cyclic hydrazones (CLVII; n = 0–6) which are formed by the reaction of 2-hydroxymethylene-3-ketoandrostanes with the hydrazides of dicarboxylic acids. These compounds are representatives of steroidal 9–15-membered heterocycles containing four nitrogen atoms[212]:



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HALOACETYLENES

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I. INTRODUCTION

This review deals with the halogenated acetylenes XC≡CH and XC≡CX, where X = I, Br, Cl, or F. The chemistry of the haloacetylenes is developing rapidly and opens wide prospects for the use of these compounds in organic synthesis. Information about this class of compounds has not been systematised and it seems desirable to make the material accumulated in this field more accessible. The review covers literature published up to November 1966.

The first acquaintance of investigators with halogenated acetylenes began in 1860, when Sawitsch[1] found that the action of alcoholic solutions of sodium ethoxide (or potassium hydroxide) on tribromoethane or heating it with solid potassium hydroxide to 100° gives, in addition to dibromoethylene, a gaseous substance which ignites spontaneously in air, attacks the eyes, and gives an explosive precipitate with an ammoniacal solution of copper(I) oxide. Somewhat later Reboul[2,3] found that it was bromoacetylene but he invariably obtained it mixed with acetylene. Pure bromoacetylene was obtained only in 1885 by Sabaneev[4]. In 1865 Berend[5] first obtained di-iodoacetylene by the reaction of silver acetylide with an ethereal solution of iodine. In 1880 Wallach[6] obtained chloroacetylene on boiling barium ββ-dichloroacrylate with barium hydroxide: he characterised the product, obtained some derivatives of C_2HCl, and found that the reaction proceeds through the intermediate formation of chloropropionic acid, which is readily decarboxylated:

$$CCl_2{=}CHCOOH \rightarrow ClC{\equiv}CCOOH \rightarrow C_2HCl + CO_2.$$

Lemoult[7] obtained dibromoacetylene in 70% yield by heating an alcoholic solution of tribromoethylene with an excess of alcoholic potassium hydroxide in a stream of nitrogen and described its properties. Dichloroacetylene was discovered in 1914: Böeseken and Carrière[8] obtained it on heating the barium trichloroacrylate. Grignard and his coworkers[9], in studying the reaction of equimolecular amounts of iodine and ethynylenedimagnesium dibromide, found a little iodoacetylene among the reaction products, in addition to the main product (up to 65%), monoiododiacetylene.

In the monohalo-substituted acetylene series fluoroacetylene was the last to be discovered. It was synthesised in two different ways: by pyrolysis of fluoromaleic anhydride and by reaction of magnesium with 2-bromo-1,1-difluoroethylene. Both methods were published by Middleton and Sharkey[10] in the USA and by Yakubovich and coworkers in the Soviet Union[11].

The first information about difluoroacetylene began to appear in the literature in 1947. In an American patent[12], which describes the preparation of perfluorinated alkynes of the type $R_FC{\equiv}CR_F$, difluoroacetylene is mentioned among the products. However, the method of making it is not described there and its physicochemical characteristics are not given. In another American patent[13], which describes the synthesis of fluoropropioloyl fluoride FC≡CCOF by the pyrolysis of difluoromaleic anhydride, difluoroacetylene is mentioned as one of the products of the pyrolysis. However, it was not isolated. The author observed only the formation of a compound of composition C_4F_4, which he took to be a dimer of difluoroacetylene. In the brief information about the preparation of difluoroacetylene[14] there is also nothing about the method of preparation, purification, and properties of the substance. Slight traces of difluoroacetylene were found among the products of the photolysis of tetrafluoroethylene[15] and of the radiolysis of hexafluoroethane[16]. According to an American patent[17], the dihaloacetylenes, including difluoroacetylene, are obtained by pyrolysis of liquid or gaseous halogenated hydrocarbons at 1200–1300°C in high vacuum. Chlorofluoroacetylene was recently obtained[18] by dehydrohalogenation of 1,1-dichloro-2-fluoroethylene at 120°C in a vacuum.

The study of the halogenated acetylenes for over a century has developed rather slowly. On the one hand, the investigations, which were not stimulated by practical requirements, were theoretical and carried out on a very limited scale. On the other hand, work with haloacetylenes is accompanied by considerable difficulty and danger since these substances ignite and explode violently on contact with air. Moreover, they exhibit comparatively high toxicity. Only with the development of appropriate experimental techniques and of contemporary physical methods of investigation were significant advances made in this field. However, bromochloroacetylene, chloroiodoacetylene, bromofluoroacetylene, bromoiodoacetylene, and iodofluoroacetylene are now known.

II. SYNTHESIS OF THE HALOACETYLENES AND SOME OF THEIR DERIVATIVES

1. Preparative Methods for Haloacetylenes

The methods at present known for the production of haloacetylenes can be classified as follows, according to the reactions on which they are based.

A. The hypohalite method is based on the fact that hypohalite in alkaline medium acts on acetylene or a substance with an acetylenic hydrogen [19]:

$$CH{\equiv}CH + 2\,OX^- \rightarrow XC{\equiv}CX + 2\,OH^-.$$

Biltz and Küppers [20], having obtained di-iodoacetylene by the reaction of alkaline hypoiodite, iodine, and acetylene, ascribe to the hypoiodite the role of oxidant in the iodination. However, iodic acid, which they used as an oxidant, seemed of low activity and such oxidants, like the free hypohalogenous acids, add to the triple bond [19]:

$$RC{\equiv}CH + 2\,HOX \rightarrow [RC(OH)_2CHX_2] \rightarrow RCOCHX_2.$$

Hypoiodites are the most active; they react almost instantaneously. Hypobromites and hypochlorites are less active, especially the latter. The rate of reaction continually decreases in this sequence and a correspondingly more alkaline medium is required to effect the reaction; hypochlorite, for example, requires concentrated alkali [21,22].

Isolated authors have modified this method to obtain dihaloacetylenes (especially C_2I_2). The production of monoiodoacetylene in this way has recently been described [23,24].

The method described above [20] is the most convenient process for the preparation of *di-iodoacetylene*:

$$C_2H_2 + KOI + I_2 \rightarrow C_2I_2 + KI + H_2O.$$

The reaction proceeds rapidly and the yield of the product is close to theoretical. Dehn's method [25] is often used for the same purpose; water, NaOCl, and KI act on calcium carbide:

$$CaC_2 + 2\,H_2O + 2\,KI + 2\,NaOCl \rightarrow C_2I_2 + Ca(OH)_2 + 2KCl + 2\,NaOH + 2KCl.$$

The yield of C_2I_2 is 80–90%. An interesting variation of the hypohalogenite method for obtaining di-iodoacetylene was proposed by Dussol [26]. He electrolysed, between platinum electrodes, an aqueous solution of potassium iodide saturated with acetylene. The iodine discharged at the anode reacts with acetylene in the alkaline medium, forming di-iodoacetylene with a current efficiency of 85%.

The same method is recommended for obtaining dichloroacetylene for demonstration experiments [27]. However, in view of the low yields this method has no preparative value [28].

B. Dehydrohalogenation of polyhaloethanes or polyhaloethylenes by alcoholic or solid alkali; this method allows both dihaloacetylenes and monohaloacetylenes to be obtained:

$$CH_2XCHX_2 + 2\,MOH \rightarrow 2\,MX + 2H_2O + HC{\equiv}CX;$$

$$CHX{=}CX_2 + MOH \rightarrow MX + H_2O + XC{\equiv}CX;$$

$$CHX{=}CHX + MOH \rightarrow MX + H_2O + HC{\equiv}CX$$

where X = Cl or Br.

Dehydrogenating agents other than alkali hydroxides can also be employed, for example, catechol potassium or sodium salts [29] and catechin [30]. Dehydrohalogenation under the action of the alkali metals [31,32] has been described; it proceeds by a radical mechanism. For example, the formation of chloroacetylene from 1,2-dichloroethylene under the action of potassium can be represented as follows [32]:

$$K + C_2H_2Cl_2 \rightarrow KCl + \cdot C_2H_2Cl$$

$$\cdot C_2H_2Cl + C_2H_2Cl_2 \rightarrow C_2HCl + HCl + \cdot C_2H_2Cl.$$

Method B seemed the most promising for the preparation of *dichloroacetylene* and *dibromoacetylene* [7,33]. The method of obtaining dichloroacetylene by the dehydrohalogenation of trichloroethylene was developed by Ott and coworkers [34]. These authors passed trichloroethylene vapour at 130° over fused and uniformly ground KOH and obtained C_2Cl_2 in 65% yield. However, explosions in the reaction tube frequently occurred. Subsequently Ott and coworkers showed [35] that the addition of 1% water glass (containing 50% silicate) to pure, solid KOH makes the procedure safe. It is noted that 10% silicate completely deactivates the KOH. According to other investigators [36], the addition of even 2% sodium silicate makes the alkali inactive.

Haloacetylenes were also obtained from certain polyfunctional halogenated compounds. Under the action of alkali such compounds liberate haloacetylene and simultaneously undergo destructive decomposition with the formation of other products. In several studies the author discusses the mechanism of such reactions. For example, according to Wagner and Pines [37] the formation of chloroacetylene in the decomposition of ββ-dichlorovinyltrichlorosilane under the influence of aqueous KOH takes place in stages, through the intermediate formation of a carbanion, which then reacts with the solvent and forms dichloroethylene or loses a chloride ion and gives chloroacetylene:

$$OH^- + Cl_3Si{-}CH{=}CCl_2 \rightarrow (CH{=}CCl_2)^- + Cl_3Si(OH);$$

$${-}CH{=}CCl_2^- + H_2O \rightarrow CH_2{=}CCl_2 + OH^-;$$

$${-}CH{=}CCl_2^- \rightarrow C_2HCl + Cl^-.$$

Under the action of alcoholic alkali dimethyldihalovinylmethanols [3,4-dihalo-2-methylbut-3-en-2-ols] decompose with the formation of acetone and monohaloacetylene [38]:

$$(CH_3)_2C(OH)CX{=}CHX \xrightarrow{HX} (CH_3)_2C(OH)C{\equiv}CX \rightarrow CH_3COCH_3 + C_2HX$$

$$(CH_3)_2C(OH)CX{=}CHX \rightarrow CH_3COCH_3 + CHX{=}CHX \xrightarrow{-HX} C_2HX.$$

According to Zincke [39], the decomposition of α-dichloromethyl-β-chlorovinyldiketone[1,1,5-trichloropent-4-en-2,3-dione] on heating with an excess of alkali in a current of hydrogen takes place as follows:

$$\begin{array}{l} CHCl_2{-}CO \quad H \qquad\quad CHCl_2{-}COH \\ ClHC{=}CH{-}CO \quad OH \rightarrow \quad CHCl{=}CHCOOH \end{array}$$

$$CHCl_2{-}COH \rightleftarrows CCl_2{=}CHOH;$$

$$CCl_2{=}CHOH + NaOH \rightarrow CCl{\equiv}CH + NaClO + H_2O.$$

C. Dehalogenation of polyhaloethanes or polyhaloethylenes by a metal was used to obtain monohaloacetylenes:

$$CX_2{=}CHX + M \rightarrow MX_2 + XC{\equiv}CH \text{ (for example, X = Br, M = Zn),}$$

$$CXY{=}CHY + M \rightarrow MY_2 + CX{\equiv}CH \text{ (for example, X = F, Y = Br, M = Mg).}$$

Viehe and Franchimont [40] proposed a preparative method for obtaining *fluoroacetylene* (yield 80%) from dibromofluoroethylene with magnesium in tetrahydrofuran.

D. Reaction of metal acetylides with halogens and some of their compounds which contain a negative group (for example, with cyanogen chloride). The halogen replaces both hydrogen atoms in acetylene, irrespective of whether one or both hydrogen atoms were substituted by metal [41]:

$$MC{\equiv}CM + 2X_2 \rightarrow 2MX + XC{\equiv}CX;\ HC{\equiv}CM + 2X_2 + MOH \rightarrow H_2O + 2\,MX + XC{\equiv}CX$$

where X = Br or I. The principal use of this method is the preparation of di-iodoacetylene [5,42–44]. Evidently another example of this type of reaction must be that described [45] between sodium acetylide and epi-iodohydrin [1,2-epoxy-3-iodopropane], [45] but the yield of C_2I_2 from this is insignificant.

E. Reaction of the same reagents as in Method D with ethynylenedimagnesium dibromide, which also leads to dihaloacetylenes:

$$BrMgC{\equiv}CMgBr + 2X_2 \rightarrow MgBr_2 + MgX_2 + XC{\equiv}CX$$

where X = Br or I.

F. The decomposition of mercury monohaloacetylides is a preparative method for obtaining *bromoacetylene* and *chloroacetylene* [46]:

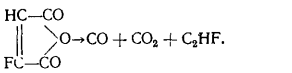
$$Hg(C{\equiv}CX)_2 + 4KCN + 2H_2O \rightarrow 2KOH + K_2Hg(CN)_4 + 2HC{\equiv}CX.$$

The initial mercury salts are readily obtained by shaking the corresponding dihaloethylenes CHX=CHX with mercury(II) cyanide in ~ 10% KOH solution:

$$2HXC{=}CXH + Hg(CN)_2 + 4KOH \rightarrow 2KCN + 2KX + 4H_2O + Hg(C{\equiv}CX)_2.$$

Fitzgibbon [47] showed that only *cis*-1,2-dichloroethylene forms a mercury bis(chloroacetylide) in this reaction. This salt liberates C_2HCl under the action of conc.HCl. *trans*-1,2-Dichloroethylene reacts with an alkaline solution of mercury(II) cyanide in another way. The author separated at least three products of the reaction, including $Hg(CCl{=}CHCl)_2$, which when boiled with conc. HCl gives dichloroethylene and $HgCl_2$.

G. The destructive decomposition of various halogen-containing compounds on heating, irradiation, etc. C_2I_2, C_2HCl, and C_2Cl_2 were obtained by heating the barium salts of iodopropiolic [48], $\beta\beta$-dichloroacrylic [6], and trichloroacrylic [8] acids respectively. The formation of C_2Cl_2 occurs in the pyrolysis of carbon tetrachloride [49]. The decomposition of dibromomuconic acid leads to the formation of C_2HBr. [50] Of the reactions of this type the most interesting from the preparative standpoint is a method of obtaining *fluoroacetylene* by the pyrolysis of fluoromaleic anhydride at 600–800°:



$$\rightarrow CO + CO_2 + C_2HF.$$

The yield of C_2HF is close to theoretical [10].

2. Synthesis of Derivatives of the Haloacetylenes

Some derivatives of haloacetylenes have been synthesised by the methods described above. Thus, Grignard and coworkers [51–53] obtained various haloacetylenes of the type RC≡CX (X = Br or I):

$$RC{\equiv}CMgX + BrCN \rightarrow MgXCN + RC{\equiv}CBr.$$

Bourguel and Truchet [54] obtained substituted chloroacetylenes by the reaction:

$$RC{\equiv}CNa + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2Na + RC{\equiv}CCl.$$

Nazarov and Bergel'son [55] synthesised 4-bromo-2-methylbut-1-en-3-yne by the dehydrobromination of *cis*-1,2-dibromo-3-methylbuta-1,3-diene:

$$CH_2{=}C(CH_3){-}CBr{=}CHBr + CH_3ONa \rightarrow NaBr + CH_3OH + CH_2{=}C(CH_3)C{\equiv}CBr.$$

The reaction of 3,3,3-trifluoro-1,2-dihaloprop-1-enes with molten sodium hydroxide at elevated temperature [56] gave 1-chloro- and 1-bromo-3,3,3-trifluoroprop-1-ynes:

$$CF_3CX{=}CHX + NaOH \rightarrow H_2O + NaX + CF_3C{\equiv}CX.$$

For X = Cl the temperature of the reaction is 280–290°C and the yield 19%; for X = Br, they are 180–190°C and 27% respectively.

Eglinton and McCrae [57] obtained 1-bromoacetylenes in 80% yields by the action of bromine on organomercury compounds:

$$(RC{\equiv}C)_2Hg + 2Br_2\,(\text{in } CCl_4) \rightarrow HgBr_2 + 2RC{\equiv}CBr.$$

Various substituted haloacetylenes RC≡CX (R = Ar, $-CH_2OH$, $-CH_2OAr$, $-CH_2OCOAr$, alkenes, etc.; X = Br, I) were obtained in yields up to 50–80% by the reaction of the corresponding copper acetylides with halides (in solvents) [58–60]:

$$RC{\equiv}CCu + X_2 \rightarrow CuX + RC{\equiv}CX.$$

Chloro-, bromo-, and iodo-acetylenes were also obtained in analogous fashion [61]:

$$LiC{\equiv}C{-}C{\equiv}CH + X_2 \rightarrow XC{\equiv}C{-}C{\equiv}CH + LiX.$$

t-Butylfluoroacetylene is obtained by the dehydrohalogenation of the fluorohaloalkenes $(CH_3)_3CHC{=}CBrF$ and $(CH_3)_3CCCl{=}CHF$. [62] We note that the last is capable of spontaneous polymerisation to form interesting products. Among these are found 1,2,3-tri-(t-butyl)trifluorobenzene and other fluorinated derivatives of the valence isomers of benzene [62,63].

Tsmur and Ivanik [64] have described an interesting preparation of bromo(diethylamino)acetylene:

$$CH_2BrCON(C_2H_5)_2 \xrightarrow{PCl_5} CH_2BrCCl_2N(C_2H_5)_2 \xrightarrow{-2HCl} BrC{\equiv}C{-}N(C_2H_5)_2.$$

The lithium, sodium, and potassium salts of chloroacetylene are obtained, as Viehe [65] showed, by the reaction of a metal amide with *cis*- or *trans*-dichloroethylene in liquid ammonia:

$$ClCH{=}CHCl + 2LiNH_2 \rightarrow LiCl + LiC{\equiv}CCl + 2NH_3.$$

3. Analytical Determination of the Haloacetylenes

Little has been published on methods of analysis of the haloacetylenes. A procedure for the quantitative analysis of bromoacetylenes has been described, based on a specific method for the liberation of a halide, which is inert to ordinary hydrolysis. Chodkiewicz and coworkers [66] give two variants of this method.

According to the first variant 1-bromoacetylene is treated with a mixture of an acetylene compound with a trace quantity of copper(II) sulphate, a reductant (hydroxylammonium sulphate), and an organic base (for example, ethylamine) in a water–methanol medium.

According to the second variant the 1-bromoacetylene reacts with $CuSO_4$ and ethylamine in the same medium. In both variants the bromine is brought into an ionic state and determined argentometrically. The results of the analysis are reproducible with an accuracy of up to 1–2%. Both variants are also applicable to the determination of iodine in 1-iodoacetylenes, but only the second variant is applicable to the analysis of chloroacetylenes.

Widmann [67] determined the concentration of dichloroacetylene by the addition of an excess of 0.1 *N* solution of iodine in CCl_4 to an ethereal solution of the C_2Cl_2. The reaction mixture was kept for 2 h in daylight, after which the free iodine was titrated with thiosulphate. The author also found that there was a linear relation between the concentration of dichloroacetylene and the refractive index, and also the density, of ethereal solutions of C_2Cl_2. [36,38] Ott employed for analysis the ability of C_2Cl_2 to react with

certain substances with the formation of a dye. For example, an ethereal solution of C_2Cl_2 was added to a hot alcoholic solution of quinaldineiodoethylate [sic]† and the blue polymethine dye formed precipitated with perchlorate. Dyes were obtained similarly with 2-methylbenzthiazole and the corresponding selenium compound[68].

III. PHYSICAL PROPERTIES OF THE HALOACETYLENES

1. General Characteristics

With the exception of fluoroacetylenes, the halogenated acetylenes have a disgusting odour.

Under ordinary conditions C_2HBr, C_2HCl, and C_2HF are colourless gases; C_2HI, C_2Cl_2, and C_2Br_2 are liquids; and C_2I_2 is a solid.

C_2HBr condenses to a colourless liquid at room temperature and a pressure of 3 atm.[3] Aqueous and alcoholic solutions of C_2HBr and C_2HCl shine in the dark and give a strong ozone reaction[69,70]. The latent heat of vaporisation of C_2HBr is 58 cal deg^{-1} [cal g^{-1}? (Ed. of Translation)], and that for C_2HCl is 89 cal deg^{-1} [cal g^{-1}? (Ed. of Translation)].[70] The vapour pressure of C_2HBr has been measured from -58.7° (27.4 mmHg) to -1.2°C (610 mmHg) and that of C_2HCl from -68.0° (111.7 mmHg) to -35.9°C (636.9 mmHg) (see Briscoe and coworkers[71]).

The vapour pressure of C_2HF has been measured at various temperatures from -150° (26 mmHg) to -109.8°C (543 mmHg) (see Viehe and Franchimont[40]). The values of some thermodynamic quantities have been calculated for C_2HF and C_2F_2 in the temperature interval from 293.15° to 6000°K: standard free energy, entropy, change in enthalpy, and equilibrium constants for dissociation or ionisation[72]. The unusually low boiling point of fluoroacetylene shows the presence in it of only weak hydrogen bonds.

Di-iodoacetylene is readily volatile even at room-temperature[73]. The values of some thermodynamic functions have been calculated for it for temperatures from 373.16° to 1000°K: enthalpy, free energy, entropy, heat capacity[74]. The crystal lattice of solid di-iodoacetylene has been studied by X-ray diffraction[75,76].

Recently similar thermodynamic functions have been calculated for C_2HBr, C_2HCl, C_2HF, and their deuterated derivatives within the temperature limits 100–2000°K in terms of rigid rotator and harmonic oscillator models. The mean vibration amplitudes for molecules of the same compounds and the molecular polarisabilities have also been calculated[77] The calculated values of the latter for C_2HBr, C_2HCl, and C_2HF were 59.3203, 50.4078, and 31.8698 cm^3 × 10^{-25}. The values found for C_2HBr and C_2HCl were 68.1559 and 56.6645 cm^3 × 10^{-25} respectively.

Lemoult's calculated heat of combustion of dibromoacetylene is 260 kcal mole^{-1} and the heat of formation 71.4 kcal mole^{-1}. Pascal[79] gives values he found experimentally for the molecular magnetic susceptibility of dibromoacetylene and dichloroacetylene: 748 × 10^{-7} for C_2Br_2 and 526 × 10^{-7} for C_2Cl_2. The calculated values are 767.5 × 10^{-7} and 548 × 10^{-7} respectively.

Table 1 gives the most important physical constants and some physicochemical properties of halogenated acetylenes.

† The exact nature of this compound is not clear in Reference 68 (Ed. of Translation).

TABLE 1. Physical properties of haloacetylenes.

Haloacetylene	M.p., °C	B.p., °C	Dipole moment, D	Solubility	
				in water	in organic solvent
Bromoacetylene	—	−2[70] 4.7±0.1[71]	0[89]	soluble[2,6,70,93]	soluble in alcohol[4,93] very soluble in $C_2H_2Br_2$[3]
Chloroacetylene	—	from −32 to −30[69] −29.6±0.1[71]	0.44[89]	soluble[69]	soluble in alcohol[69]
Iodoacetylene	—	32[9]	—	—	—
Fluoroacetylene	from −165 to −160[11]	−104[11] −104.3[40] −105[87]	0.75±0.01[90] 0.73[91]	insoluble	soluble in diethyl ether
Di-iodoacetylene	74[80,81] 77–78[82,83] 78[45,73] 78.5–78.9[44] ~80[86] 81[35,43,82] 82[84–86]	98/4 mmHg (decomp. with explosion)[44]	0.33·10^{-18} e.s.u.[92]	insoluble[44]	soluble in ordinary organic solvents[43,73,80]
Dibromoacetylene	from −25 to −23[10]	76[33] 76–76.5[88] 80[7]	—	insoluble[7]	soluble in many organic solvents[7]
Dichloroacetylene	from −68 to −64[21] from −66 to −64.2[10]	32[21] 32–33/748 mmHg[5]	— —	insoluble insoluble	soluble in tetrachloroethane[24]; diethyl ether[21,24]

Note. The superscripts denote literature references.

2. Combustibility and Explosibility

Most of the halogenated acetylenes studied are capable of spontaneous ignition in air and also on heating. Often on contact with atmospheric oxygen they explode with great violence which makes it difficult and hazardous to work with them. *Bromoacetylene* burns in air with a purple smoky flame[1–3,50]. With pure oxygen it explodes with a flame and copious liberation of carbon[3]. Some authors[71] consider that C_2HBr cannot be mixed with oxygen at elevated pressure without explosion. *Chloroacetylene* also ignites and explodes on contact with air[6,46,69,94]. When insufficiently diluted with hydrogen it explodes with the formation of carbon; with insufficient air it inflames and burns with deposition of soot. The lower explosion limits with oxygen at 100°C are: for C_2HCl, 0.6–2.0 mmHg pressure, and for C_2HBr 2.5–4.5 mmHg. The presence of argon, nitrogen, and helium affect this limit for C_2HCl. The ignition of C_2HBr is inhibited by the addition of CS_2, C_2H_4, or SO_2.[71] In the gas phase fluoroacetylene is stable in air and only on setting fire to a stream of the gas does it burn, with a blue flame[10,11,40]. Viehe and Franchimont[40] reported that they did not observe explosions with C_2HF in any state of aggregation. Other investigators[10,87] showed that liquid fluoroacetylene exploded violently but the reasons are not clear. These reports are confirmed by experiments made by the authors of the present review. It has been stated[10] that solid C_2HF does not explode. *Di-iodoacetylene* decomposes to the elements with a powerful explosion on heating to 80–100°C.[87,95] According to other work, decomposition with explosion sets in between 121° and 128°C; the explosion of C_2I_2 has also been noted on vacuum distillation (4 mmHg, 98°C).[44] Jaeschke[96] reported the explosion of the dry product in work after Franzen. C_2I_2 bursts into flame sometimes even at low temperatures[44] and explodes on mechanical shock or friction. An example has been described of a violent explosion with a serious wound in an

attempt to spread crystals of C_2I_2 with a pestle[97]. *Dibromoacetylene* takes fire in air and burns with a red, smoky flame[88]; it explodes very violently on heating, decomposing with formation of carbon[7,19], and also on coming in contact with oxygen; it even explodes in an atmosphere of CO_2 or N_2 containing traces of oxygen[33]. *Dichloroacetylene* explodes violently on contact with air[19,34], and also on moderate heating[19]; diluted with nitrogen, it ignites in air[98]. Out of contact with air it decomposes with explosion at 130°C.[27]

3. Physiological Activity

Nothing has yet been published about the toxicity of iodoacetylene and fluoroacetylene. All the other mono- and di-haloacetylenes known at present are substances which exhibit comparatively high toxicity. Sabaneev[4] and Nef[93] compare bromoacetylene with phosphorus in toxicity. Ingold[69] states that inhalation of even traces of chloroacetylene produce very unpleasant sensations. Di-iodoacetylene vapour strongly attacks the eyes[43] and mucous membranes[1,73]; it is a strong poison for micro-organisms and an effective inhibitor of putrefraction, its activity to it being approached only by the extremely toxic cyanogen iodide[73], but it does not find use in the fight against putrefraction owing to its high toxicity and disgusting odour. Mebert[99] found that subcutaneous introduction of 0.2–0.3 g di-iodoacetylene into rabbits weighing 1.5–2.0 kg was lethal in two days bringing about emphysema. Loew[100] studied the toxic action of di-iodoacetylene in dilutions of 1 : 5000, 1 : 10 000, 1 : 20 000, 1 : 100 000, and 1 : 1 000 000 on bacteria (*Bac. subtillis, Bac. fluorescens liquefaciens*), fungi (spores of penicillin, *Aspergillus*), yeasts, lower algae (diatoms, *Oscillarien*, *Spirogyrafäden*), the infusoria *Flagellaten*, and also *Zimnaen*, *Copepoden*, *Nematoden*, and *Rotatorien*. The author found that in the presence of di-iodoacetylene, even in very great dilutions, all the micro-organisms did not develop, but either lost mobility, or usually perished. Of the vertebrate animals, they made tests on mice and porpoises. When introduced subcutaneously or *per os*, C_2I_2 acts slowly, owing to its poor solubility, but inhalation of its vapour leads to rapid destruction of the animals.

Inhalation of dibromoacetylene produces a severe, long-lasting headache[33,88], a sensation of weakness[88], difficulty in breathing, and pronounced loss of memory[33].

Dichloroacetylene shows its toxicity quite specifically[68]. On inhaling the ether addition compound of dichloroacetylene mice died from respiratory paralysis[35].

Ott and Bossaller[101] have shown, in a work devoted to the chemical reactions of dichloroacetylene, that "lower aliphatic alkylchloroacetylenes are evidently very toxic compounds, the action of which brings about prolonged disturbance of the nervous system. It appears in weakness of the legs, maintained for a week, and for some time walking is generally impossible. Temporary paralysis of the optic nerves also occurs".

4. Structure of the Molecule. Spectra

Nef[43,93] thought that the mono- and di-haloacetylenes have not a linear, but an acetylidene structure: XHC=C or X_2C=C, with a bivalent carbon atom, which also confers specific properties on these compounds. Such a view was held subsequently by Lawrie[33], and by Nekrasov[88]. Other investigators — Lemoult[102], Ward[103], Biltz[104], and Ott[34] — supported a linear structure for the haloacetylenes, chiefly on the basis of a study of their chemical properties. According to Ingold[69] the monohaloacetylenes are tautomeric compounds, since the acetylenic hydrogen atom is labile: $XC{\equiv}CH \rightleftharpoons XHC{=}C$. The properties of chloroacetylene which sharply distinguish it from acetylene, he explains by the fact that in chloroacetylene (and also in bromoacetylene) this equilibrium at ordinary temperatures is more displaced to the side of acetylenic structures than in acetylene. The dihaloacetylenes, according to Ingold, exhibit stable acetylene structures. Howell and Noyes[105] considered that the properties of di-iodoacetylene are readily explained if it is assumed that the iodine atoms in this compound are positive, and it is not necessary to resort to Nef's bivalent carbon atom.

In later work objections against the acetylidenic structures were based on the results of studies of the haloacetylenes by physical methods. Thus, Sidgwick[106] doubted the existence of acetylidenic structures on the basis that the terminal carbon in such molecules only has a valency sextet. He considers that the controversy about the structure of di-iodoacetylene was settled in favour of the linear structure of its molecule since the dipole moment of this compound was found to be 0.33 D, that is, closer to zero. Glockler and Morrel[107] initially favoured the linear structure on the basis of a study of the Raman spectrum of di-iodoacetylene in alcoholic solution, but in later work[108] supported a non-linear structure for this compound. However, Cleveland and Meister[109], on comparing their results from an investigation of the vibrational spectrum of di-iodoacetylene with data of other authors, again supported the linear, symmetrical structure for this compound. There have been other investigations of the spectra of di-iodoacetylene[110-112]. Table 2 gives some of the results obtained in these investigations.

de Laszlo[119] studied the structure of C_2I_2, C_2Br_2, and C_2Cl_2 by electron diffraction in the gas phase and concluded that the first two compounds had linear structures. However, he thought that the experimental results agreed with the acetylidene structure for dichloroacetylene. An investigation of the radial distribution curve led him to the conclusion that dichloroacetylene is a mixture with $\geq 20\%$ molecules with a linear structure. de Laszlo thought that a difference in the structure of C_2Cl_2 may also appear in some of its chemical properties. For example, C_2Cl_2, unlike di-iodo- and dibromo-acetylene, invariably explodes on contact with air, forms carbonyl chloride on oxidation, etc.

The results of other authors who investigated dichloroacetylene by the same method completely disagree with those of de Laszlo. Thus Hassel and Viervoll[123] found de Laszlo's conclusion about the C_2Cl_2 structure erroneous, and on the basis of an analysis of the experimental data they concluded that its molecule is linear, symmetrical, and corresponds to the formula Cl–C≡C–Cl. Hassel and Taarland[120] came to the same conclusion, and also Finbak and Hassel[121], who also studied the molecular structure of C_2Cl_2 by electron diffraction.

The linear structure of bromoacetylene and chloroacetylene was demonstrated by electron diffraction[23]. Microwave spectroscopy confirmed the linearity of the molecules of chloroacetylene[115] and showed an analogous structure of fluoroacetylene[23].

The structure of iodoacetylene has not yet been studied.

The infrared spectra of all the monohaloacetylenes are now known. The infrared spectra of gaseous C_2HF, C_2HBr, C_2HCl, and their deuterated derivatives have been studied and published in the detailed review of Hunt and Wilson[23] and more recently also by Nagarajan and Hariharan[77]. Brown and Tyler[24] investigated the infrared spectra of C_2HF, C_2DF, and C_2HI. Other authors[10,11,40] have also considered the infrared spectrum of fluoroacetylene.

Displacement of the bond frequencies to longer wavelengths is observed in the infrared spectra of deuterated monohaloacetylenes. The force constants of the C–halogen bonds in these molecules are considerably greater than in the corresponding haloethanes and are essentially the same as in the cyanogen halides, but the C–halogen bond length is much (~ 10%) shorter than in the corresponding haloethanes and a little greater than the same bonds in the cyanogen halides[23].

White observed the $J = 1 \rightarrow 2$ transition taking place in the microwave spectrum of DC≡CCl obtained with the aid of a spectrometer of high resolution, and found a hyperfine structure, due to the quadrupole moment of the deuterium. He measured the constants of quadrupole interaction of deuterium, 175 ± 20 kHz, calculated the field gradient at the deuterium nucleus, $q = (8.85 \pm 0.9) \times 10^{-14}$ e.s.u., and discussed the results obtained[124,125].

The bond lengths in the haloacetylene molecules were calculated from the results of microwave spectroscopy[91], but chiefly from the investigation of these substances by electron diffraction. Table 2 gives the vibration frequencies found in the infrared spectra of halogenated acetylenes and also the calculated values of the lengths and force constants of the bonds in these molecules according to the work of various authors. The Stark effect which can be observed in the microwave spectrum of C_2HCl was close to that calculated[115].

Bykov[126] proposed a scheme for calculating the electronic charges of the bonds, starting from the values of the electronegativities of the atoms and calculated the σ- and π-electron charges of the bonds in the chloroacetylene molecule; such a calculation gives:

$$\underset{0.91}{\overset{1.91}{H}} \quad \underset{2.00}{\overset{2.00}{C^{2\pi}}} \quad \underset{2.00}{\overset{2.09}{C^{2\pi}}} \quad \underset{1.09}{\overset{}{Cl}}$$

(the lower row is for π-electrons).

Anno and Sado[127] found that the relation between the length and order of the C–Cl bond in the chloroacetylene molecule is expressed by a relation similar to that given earlier by Coulson for C–C bonds[127].

Analysis of the infrared and microwave spectra for chloroacetylene led some investigators to conclude that the C–Cl bond has some degree of double-bond character, which explains the resonance of the

$$H-C\equiv C-C \quad \text{and} \quad H-\overset{-}{C}=C=\overset{+}{Cl}$$

structures[113,115]. Comparison of chloroacetylene with methyl chloride shows that on going to chloroacetylene the length of the C–Cl bond decreases from 1.786 Å (in CH_3Cl) to 1.632 Å (in C_2HCl). During this the force constant of this bond rises sharply, by approximately 45%. In analysing this fact, Duchesne[118] finds that the concept of resonance is here insufficient, since it can explain the increase in the force constant of the bond to the extent of only ~ 15%. The author assumes that this phenomenon is explained by the large value of the overlap integral of the chlorine and carbon orbitals.

An analogous tendency also appears in the C–F bond in fluoroacetylene[23,24,40]. See Moreau[128] for the electronic structure of C_2HF and C_2HCl.

TABLE 2.

Haloacetylene	Bond frequencies found in the infrared and Raman spectra, cm^{-1}			Lengths of the bonds in the molecule, Å			Force constants of the bonds in the molecule, 10^{-5} dyn cm^{-1}		
	C–H	C≡C	C–X	C–H	C≡C	C–X	C–H	C≡C	C–X
Bromoacetylene	3325[23]	2085[23]	618[23]	1.0587[23,114]	1.20±0.04[89]	1.80±0.03[89]	5.85[23,122]	15.7[23]	4.6[23]
Chloroacetylene	3340[23] 3319[113]	2110[23] 2109[113]	756[23,113]	1.0587[23,114] 1.052±0.001[115]	1.211±0.001[23] 1.21±0.04[89] 1.211[115,117,118]	1.632±0.001[115] 1.68±0.04[89] 1.630[118]	5.85[23,122]	15.8[23] >15.0[118]	5.4[23] 5.0[118]
Iodoacetylene	3320[24]	2075[24]	about 629[24]	1.055[116]	1.203[116]	1.988[116]			
Fluoroacetylene	3330[10,11] 3333[40]	2210[10,11] 2255[23]	1000—1100[10,11]	1.0587[23,114]	1.2054[23]	1.275[23]		15.85[23,114]	8.8[23]
		2245[24]	1055[23]		1.198[90]	1.279[90]	5.85[23,122]	15.8[24]	
	3355[23]	2092	1064[24]	1.053[90]		1.280[40]	6.06[24]		8.64[21]
	3370[24]	2118 2247 2222 [40]	1052,1077[40]		1.20[23]				
Di-iodoacetylene	—	2109[107]	627[107]	—	1.18[74,119]	2.03[74,119]	—	—	—
Dibromoacetylene	—	—	—	—	1.18[119]	1.84[119]	—	—	—
Dichloroacetylene	—	—	—	—	1.195[120,121] 1.18[119]	1.64[120] 1.640[121] 1.75[119]	—	—	—

Note: The superscripts denote literature references.

IV. CHEMICAL REACTIONS OF THE HALOACETYLENES

All the haloacetylenes are very reactive substances. They vigorously add halogens and various nucleophilic reagents, and polymerise. Monohaloacetylenes enter into reactions which depend on the presence of a labile acetylenic hydrogen atom. Thanks to the displacement of electrons towards the electronegative halogen atoms, the hydrogen in such compounds is more protonic than in acetylene. For this reason it readily reacts with substances of basic character.

As already mentioned, Howell and Noyes [105], in objecting to the acetylidenic structure of Nef, expressed an opinion about the positive nature of the halogen in the haloacetylene molecules. Although the conclusions advanced by the authors on this basis are quite controversial and on the whole do not constitute a sufficiently weighty argument, such a standpoint is firmly based, bearing in mind the strong *I*-effect of the C≡C group. The latter can be shown as follows.

Petro [129] considered the problem of the influence of hybridisation of the carbon atom on bond polarity. On going from sp^3-hybridisation to sp^2- and sp- the electronegativity of the carbon atom rises appreciably. This leads to a corresponding rise in the dipole moment of the H–C bond:

$$\text{H—C}\,(sp^3) = 0.31$$
$$\text{H—C}\,(sp^2) = 0.63$$
$$\text{H—C}\,(sp) = 1.05.$$

The prediction of the direction of polarisation of the C–halogen bond in haloacetylene molecules (sp-hybridisation) is especially interesting. Let us consider, for example, chloroacetylene. The dipole moment of the chloroacetylene molecule is 0.44 D. The dipole moment of the H–C bond in C_2HCl is 1.05 D. Since the dipole moment of the molecule is significantly lower than the dipole moment of the H–C bond, then starting from the fact that the dipole moment of a molecule is the vector sum of the ≡C–H and ≡CCl moments, it can be concluded that in the chloroacetylene molecule, which has a linear structure, the direction of the Cl–C vector is opposite to the H–C vector, that is, the bond has the character $\equiv\bar{C}-\dot{C}l$. Analogous discussions are evidently also correct for C_2HBr and C_2HF.

It is known that compounds with positively charged halogen atoms exhibit certain specific physical and chemical properties [130,131], which are also encountered in the haloacetylenes. Thus, the haloacetylenes are of low stability and readily decompose with explosion. Di-iodoacetylene displaces iodine from a solution of potassium iodide, the iodine atom is replaced by hydrogen on hydrolysis, and oxidises phenylhydrazine with release of nitrogen. Some other reactions of haloacetylenes [132,133] can also be explained from the standpoint of the concept of the positive nature of the halogen atom.

We considered it desirable to classify the reactions of haloacetylenes as follows: (1) reactions at the triple bond; (2) reactions with replacement of hydrogen; (3) reactions with replacement of halogen; (4) decomposition of the haloacetylenes, and oxidations; (5) molecular compounds of haloacetylenes.

1. Reactions at the Triple Bond

a. Reactions with halogen and hydrogen halides. Bromoacetylene [2,3], chloroacetylene [6,19,39], and fluoroacetylene [10,11] react vigorously with bromine, adding two molecules of the latter:

$$CH \equiv CX + 2Br_2 \rightarrow CHBr_2 - CXBr_2.$$

Bromoacetylene adds HI and HBr, the latter forming *trans*-dibromoethylene [134]. An American patent [135] stated the possibility of obtaining fluoro-compounds by the reaction of chloroacetylene with HF in the presence of BF_3 at 70–250°C, but the composition of the products formed was not given.

Di-iodoacetylene, on adding on free chlorine and bromine at the triple bond, also exchanges both iodine atoms during this. For example, hexachloroethane is obtained in good yield in the reaction of chlorine with solid di-iodoacetylene [44,105] or on passing dry chlorine into a chloroform solution of this substance [73]. On standing for many days with bromine in a sealed glass vessel, C_2I_2 is converted into hexabromoethane [73]. In chloroform solution at ~ 0°C, bromine is added immediately. The product is a mixture of ICBr=ClBr (80%), CI_2=ClBr (10%), and CBr_2=CBrI (10%).[43] On treatment with an ethereal solution of iodine, di-iodoacetylene is smoothly converted into periodoethylene [43]. The solvent and temperature play an important part in this. For example, in benzene the reaction takes place on heating for 1 h; [44] in boiling toluene the addition of two atoms of iodine is instantaneous [20,73]. However, equivalent quantities of iodine and di-iodoacetylene in carbon disulphide combine (in the absence of light) only after several days [73,136]. The reagent is greatly inhibited by oxygen [137].

Under the action of bromine (without a solvent or in ether) dibromoacetylene is converted into tetrabromoethylene in 89% yield [19,88]. One molecule of iodine is also added, being converted into symmetrical dibromodi-iodoethylene in 82.5% yield [19]. Hydriodic acid gives both dibromoiodoethylene CBrI=CHBr and dibromodi-iodoethylene. If the HI is not purified from free iodine, then only the latter of these products is obtained in practice [33].

Dichloroacetylene adds elemental chlorine to form hexachloroethane. With bromine water, tetrabromodichloroethane is obtained [19]. With elemental bromine, without a solvent or in carbon tetrachloride medium, dichloroacetylene gives *sym*-dibromodichloroethylene [34]. It slowly reacts with a dilute ethereal solution of iodine, adding on one molecule of iodine and forming dichlorodi-iodoethylene [34,35]. The same reaction proceeds rapidly in carbon tetrachloride [35].

b. Reactions with ammonia and amines. Chloroacetylene does not react with ammonia. With diethylamine in diethyl ether it slowly forms diethylformamide and diethylammonium chloride. It reacts with aniline only at 150–160°C, forming anilinium chloride and indole [138]. Fluoroacetylene reacts with liquid ammonia forming ammonium fluoride and acetonitrile. According to Viehe and Franchimont [40] the mechanism of the reaction is the nucleophilic addition of amide ions at the triple bond with subsequent elimination of a fluoride anion: the intermediate formation of aminoacetylene is proposed:

$$FC\equiv CH \xrightarrow{NH_3} \left[H_2N-C(F)=C^-\right] \longrightarrow NH_2C\equiv CH \longrightarrow CH_3CN.$$

Dichloroacetylene in ethereal solution reacts with gaseous ammonia, forming ammonium chloride and chloroacetonitrile in good yield. The intermediate formation of chloroaminoacetylene is proposed [139]:

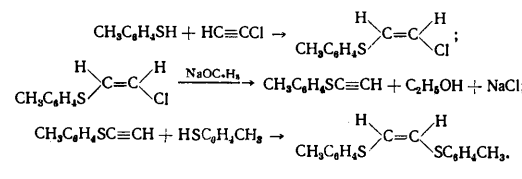
$$ClC\equiv CCl + NH_3 \rightarrow ClCH=C(NH_2)Cl \xrightarrow{-HCl} ClC\equiv CNH_2 \rightarrow CH_2ClC\equiv N.$$

With primary amines dichloroacetylene forms, in addition to the hydrochloride of the base, aminoamidines in good yield[139], analogous to those obtained earlier by other authors from tetrabromoethane or trichloroethylene with aniline and other aromatic amines[140,141]. With diethylamine the asymmetric 2-chloro-1,1-bis(diethylamino)-ethylene is formed[138]:

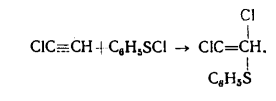
$$(C_2H_5)_2NH + ClC{\equiv}CCl \rightarrow (C_2H_5)_2NCCl{=}CHCl;$$
$$(C_2H_5)_2NCCl{=}CHCl + (C_2H_5)_2NH \rightarrow HCl + [(C_2H_5)_2N]_2C{=}CHCl.$$

The passage of dichloroacetylene into an excess of triethylamine gave a quaternary ammonium salt which was converted into the perchlorate and the hexachloroplatinate(IV); a compound with gold(III) chloride was also characterised[139].

c. Reactions with sulphur-containing, mercury-containing, and other reagents. In the presence of the $C_2H_5O^-$ ion chloroacetylene adds *p*-tolylthiol to form *cis*-1,2-bis-(*p*-tolylthio)ethylene (77.4%) and *cis*-1-chloro-2-(*p*-tolylthio)ethylene (20.3%). Traces of *p*-tolylthioacetylene are also formed[142]. The initial addition product *cis*-1-chloro-2-(*p*-tolylthio)ethylene is converted, as a result of dehydrohalogenation, into *p*-tolylthioacetylene, which then also reacts with the *p*-tolylthiol. During this there is trans-nucleophilic addition of the latter at the triple bond with formation of *cis*-1,2-bis-(*p*-tolylthio)ethylene[143]:



Such a reaction mechanism is confirmed by the fact that treatment of *cis*-1-chloro-2-(*p*-tolylthio)ethylene with sodium ethoxide in alcohol gives *cis*-1-ethoxy-2-(*p*-tolylthio)ethylene[144]. The reaction of chloroacetylene with benzenesulphenyl chloride[145] in ether gave *trans*-1,2-dichloro-2-phenylthioethylene in 38% yield:



The reaction of fluoroacetylene with thiophenol proceeds by nucleophilic addition of the latter with formation of 1-fluoro-1-phenylthioethylene[146]. The addition of thiophenol to dichloroacetylene in alcoholic–ethereal solution gave *cis*-1,2-dichloro-2-phenylthioethylene, in addition to *cis*-1,2-dichloro-2-ethoxyethylene as a side-product[145]. In the presence of alkoxides, dichloroacetylene adds alcohols without loss of halogen, forming $\alpha\beta$-dichlorovinyl esters[139]:

$$CCl{\equiv}CCl + ROH \rightarrow HCCl{=}CClOR.$$

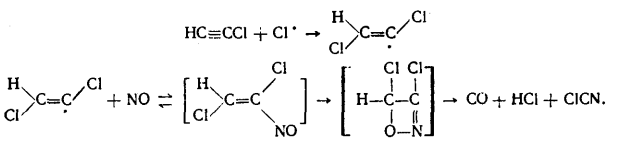
Chloroacetylene, on reacting with an aqueous solution of mercury(II) chloride, gives tris(chloromercury)acetic acid $(ClHg)_3CCO_2H$.[46] The following mechanism for the reaction is proposed:

$$HC{\equiv}CCl + 2\,ClHg^+ + 2\,Cl^- = (ClHg)_2CHCCl_3 \xrightarrow{-HCl} \xrightarrow{+ClHg^+ + Cl^-}$$
$$\rightarrow (ClHg)_3CCl_3 \xrightarrow{H_2O} (ClHg)_3COOH.$$

Sherwood and Gunning[147] described an interesting reaction of chloroacetylene with nitrogen monoxide, induced by a chlorine radical, leading to the breaking of the triple carbon bond:

$$HC{\equiv}CCl + NO \xrightarrow{Cl^\cdot} ClCN + CO + HCl.$$

The authors irradiated a rarefied mixture of C_2HCl, NO, and $COCl_2$ (a source of chlorine radicals) with radiation from a quartz mercury lamp at room temperature through a filter which cuts off the short waves. They give a reaction mechanism with hypothetical formation of an intermediate product of cyclic structure:



When chloroacetylene served as the source of radicals diacetylene was also found in the products:

$$C_2HCl \xrightarrow{+h\nu} C_2H^\cdot + Cl^\cdot$$
$$C_2H^\cdot + C_2HCl \rightarrow C_4H_2 + Cl^\cdot.$$

On passing fluoroacetylene into a neutral solution of potassium tetraiodomercurate(II) HgI_2 adds at the triple bond and forms, in over 90% yield, bis-(2-fluoro-2-iodovinyl)-mercury — white, well-formed crystals, m.p. 97°C:[148]

$$FC{\equiv}CH + HgI_2 = (FIC{=}CH)_2Hg.$$

Dichloroacetylene reacts vigorously with sodium ethyl malonate. A solution of dichloroacetylene in diethyl ether is used for the reaction. The reaction mixture contains chloroethylenebismalonic ester [sic] plus a variable amount of its hydrogenation product. In an analogous reaction with the sodium derivative of diethyl ethylmalonate the main reaction product was diethyl (chloroethynyl)ethylmalonate $ClC{\equiv}C.C(C_2H_5)(CO_2C_2H_5)_2$ (~ 55%). About 33% tetraethyl chlorovinylenebis(ethylmalonate) $(C_2H_5OCO)_2C(C_2H_5).CH{=}CCl.C(C_2H_5)(CO_2C_2H_5)_2$ was also obtained; the residue (12%) was a mixture of the ester of α-methylbutyric acid (80%) and the ester of α-chlorovinylbutyric acid (20%).[139] Dichloroacetylene reacts sluggishly with diazoacetic ester; the product isolated corresponded to the empirical formula $C_{10}H_{12}N_4Cl$, but was not studied further[101]. 1,2-Dichloro--1-nitroethylene was obtained in good yield by the addition of NO_2 to dichloroacetylene[101]; the mechanism of this reaction has not been studied. The action of NO_2Cl (in ether) leads to 1,1,2-trichloro-2-nitroethylene[149]. The reaction of dichloroacetylene with thiocyanate in ether gave 1,4-bis-thiocyanatobut-2-ene in 80% yield; the mechanism of this reaction also has not been explained[150].

d. Polymerisation. Monohaloacetylenes are trimerised into symmetrical trihalobenzenes, but the yields are usually low. The main mass of the product consists of polymers whose structure has not been investigated.

Gaseous bromoacetylene does not polymerise but the liquid does. The polymerisation is catalysed by light and a molecular compound of composition $[(C_6H_5)_3P]_2NiBr_2.n\text{-}C_4H_9Br$.[151] In the liquid phase under the action of light it yellows and becomes turbid in a few hours, but after a month it has become almost completely converted into turmeric-coloured powder, only partly soluble in organic solvents. Tribromobenzene amounts to ~ 10% of the polymerisation products[4].

The copolymerisation of C_2HBr with vinyl acetate was effected in sealed glass ampoules, the reaction mixture

being kept in bright sunlight for 11 days [152]. The product was a brown amorphous substance soluble in chloroform and acetone. The copolymer decomposes at 101–102°C and by analysis it corresponds to the composition $[(CH_3COOCHCH_2)(CHCBr)]_n$. Copolymerisation with styrene was carried out similarly. The reaction products isolated were coloured solids, which by analysis and molecular weight corresponded to copolymers of composition $[(C_6H_5CHCH_2)(CHCBr)]_2$; $[(C_6H_5CHCH_2).(CHCBr)]_2$; $[(C_6H_5CHCH_2)_4(CHCBr)]_3$. [152] The reaction of C_2HBr with octacarbonylcobalt gave a solid infusible substance corresponding to the empirical formula $C_3H_3BrCoO_6$. [151]

On illumination and heating with a 100 W lamp, chloroacetylene polymerises even in the gaseous state. It gives, together with 1,3,5-trichlorobenzene, a polymer which decomposes at 290°C. [69,153]

Fluoroacetylene polymerises spontaneously at room temperature in the absence of polymerisation initiators, whether in the light or whether in the dark [11], forming a brown powder [10,11] soluble with difficulty in organic solvents. The solubility of the polymer shows its linearity, and the colour its polyene, conjugated structure [11]. A little *sym*-trifluorobenzene is also formed [10]. Dichloroacetylene is converted into resinous products and hexachlorobenzene at a temperature below 130°C. [27] Hexachlorobenzene is also formed, together with other products, in diethyl ether under the action of light or in heating the solution on the water-bath under pressure [139]. Other authors [19] maintain that dichloroacetylene is insensitive to light.

2. Hydrogen Exchange

Bromoacetylene and chloroacetylene form copper salts with solutions of copper(I) oxide in ammonia. Copper bromoacetylide is evidently unstable and is converted into copper acetylide [13,50]. Copper chloroacetylide is more stable although it changes rapidly in air: the concentration of copper in it is 9% in excess of theoretical. Under the action of HCl or KCN the substance liberates chloroacetylene, which shows the structure to be ClC≡CCu. [6,46] Silver chloroacetylide is obtained similarly [6,32,39,46,69], and also releases C_2HCl under the action of HCl and KCN. The copper and silver salts of chloroacetylene explode more violently than the corresponding salts of acetylenes, especially the silver salt, which explodes even under water [69]. The lithium salt of chloroacetylene is obtained by the reaction of *cis*- or *trans*-1,2-dichloroethylene with lithium amide, and also with organolithium compounds, for example, with n-butyl-lithium in absolute ether [154,155]:

$$CHCl{=}CHCl + LiC_4H_9 \rightarrow C_4H_{10} + CCl{\equiv}CH + LiCl;$$
$$CCl{\equiv}CH + LiC_4H_9 \rightarrow C_4H_{10} + CCl{\equiv}CLi.$$

The mercury salts of bromoacetylene and chloroacetylene $(BrC{\equiv}C)_2Hg$ and $(ClC{\equiv}C)_2Hg$, in distinction from the chlorovinyl compounds, do not exhibit the properties of quasicomplexes. They are indifferent to the action of triphenylphosphine; aqueous and alcoholic solutions of potassium cyanide or potassium iodide bring about only hydrolysis (alcoholysis) of these substances with release of the haloacetylene:

$$(BrC{\equiv}C)_2Hg + 2H_2O + 4I^- \rightarrow 2\,BrC{\equiv}CH + HgI_4^{2-} + 2\,OH^-$$

but do not lead to the liberation of elemental carbon [156]. With an aqueous solution of silver nitrate, fluoroacetylene forms only a yellow salt, also extremely explosive on heating or friction [10,11].

Deuterated derivatives of monohaloacetylenes BrC≡CD, ClC≡CD, and FC≡CD were obtained by repeatedly passing C_2HBr, C_2HCl, and C_2HF through weakly alkaline D_2O and were purified by distillation. The exchange of hydrogen by deuterium reached 70%. [23,90]

3. Halogen Exchange

The bromine atom in bromoacetylene is replaced by copper on reaction with an ammoniacal solution of copper(I) oxide. The formation of copper acetylide is proved by the production of pure acetylene when this precipitate is treated with HCl. [50] Reboul describes the decomposition of bromoacetylene in the initial stage of this reaction by the equation:

$$C_2HBr + 3\,Cu_2O \rightarrow C_2HCu_3 + CuBr + 3\,CuO.$$

Zavgorodnii and Petrov assume that in the reaction of bromoacetylene with sodium trialkyltin in liquid ammonia the lability of the hydrogen atom in the C_2HBr molecule exceeds the lability of the bromine atom. As a result of the reaction the authors obtained trialkyl(bromoethynyl)-tin(IV), together with μ-ethynylbis(trialkyltin): [157]

$$HC{\equiv}CBr \xrightarrow{R_3SnNa} R_3SnC{\equiv}CBr \xrightarrow{R_3SnNa} R_3SnC{\equiv}CSnR_3$$

where R = CH_3, C_2H_5.

Study of the reactions of dichloroacetylene showed that the first chlorine atom undergoes various reactions very readily. Its activity in reactions with ammonia and amines is comparable with the activity of chlorine in acid chlorides [139], and Viehe [154] speaks of them as "positive, capable of being replaced by metal". Under the action of alcoholic potassium hydroxide dichloroacetylene is partly converted into chloroacetylene and potassium hypochlorite. Arens [132] presents this reaction as a nucleophilic substitution of a hydroxide ion for the chloroacetylide ion at the chlorine:

$$ClC{\equiv}CCl + OH^- \rightleftarrows ClC{\equiv}C^- + OHCl;$$
$$ClC{\equiv}C^- + H_2O \rightleftarrows ClC{\equiv}CH + OH^-.$$

With organolithium compounds dichloroacetylene almost quantitatively exchanges the chlorine atom for lithium with the formation of a lithium salt of chloroacetylene [65]:

$$RLi + ClC{\equiv}CCl \rightarrow RCl + LiC{\equiv}CCl.$$

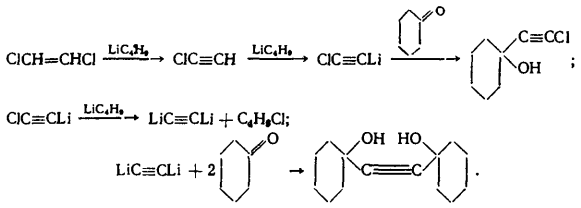
With the aid of such salts a chloroethynyl group has been introduced into the molecules of various organic compounds [65], for example:

$$LiC{\equiv}CCl + CH_3CH_2CHO \rightarrow CH_3CH_2CH(OH){-}C{\equiv}CCl;$$
$$2\,NaC{\equiv}CCl + Br(CH_2)_6Br \rightarrow 2\,NaBr + ClC{\equiv}C(CH_2)_6{-}C{\equiv}CCl;$$
$$NaC{\equiv}CCl + (C_6H_5)_3SnCl \rightarrow NaCl + (C_6H_5)_3Sn{-}C{\equiv}CCl.$$

In the decomposition of LiC≡CCl by water chloroacetylene is formed in 85% yield [154]; by the carbonisation of this salt chloropropiolic acid is obtained; reaction with orthocarbonic ester gives the ethyl ester of this acid, and with aliphatic acid anhydrides chloroethynylketones [155] are formed:

$$ClC{\equiv}CLi + (C_2H_5CO)_2O \rightarrow ClC{\equiv}CCOC_2H_5 + C_2H_5COOLi.$$

Reactions between cyclohexane and LiC≡CCl show that both chlorine atoms in dichloroacetylene can be successively replaced by lithium[155]:



With silver nitrate in water or alcohol, dichloroacetylene forms a precipitate sensitive to light, apparently consisting of C_2Ag_2 and AgCl.[19] Dichloroacetylene and also di-iodoacetylene replace both halogen atoms on reaction with Ilosvay solution. The first gives Cu_2C_2,[19] the second a mixture of Cu_2I_2 and Cu_2C_2.[42]

Exchange of the halogen atoms in reactions with organometallic compounds is characteristic for all the haloacetylenes.

With ethylmagnesium iodide bromoacetylene forms ethynylenedimagnesium dibromide[132]:

$$HC{\equiv}CBr + 2\,C_2H_5MgBr \rightarrow BrMgC{\equiv}CMgBr + C_2H_5Br + C_2H_6.$$

Fluoroacetylene reacts to form alk-1-ynes[87]:

$$2\,FC{\equiv}CH + 2\,RMgBr \rightarrow MgBr_2 + MgF_2 + 2\,RC{\equiv}CH$$
$$FC{\equiv}CH + RLi \rightarrow LiF + RC{\equiv}CH.$$

With butyl-lithium and phenyl-lithium, hex-1-yne and phenylacetylene are obtained respectively[40]; alkynes are also obtained with many other alkyl-lithiums or Grignard compounds (R = CH_3, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, $CH_2C_6H_5$).

Dichloroacetylene reacts readily with organomagnesium compounds with the formation of 1-alkyl- or 1-aryl-2-chloroacetylenes of the general formula ClC≡CR. In this way 2-chloro-1-phenylacetylene was obtained in yields of 70% and other 2-choroacetylenes in yields of 40–52% (R = *p*-tolyl, *p*-anisyl, cyclohexyl, dodecyl)[101], and also various unsaturated compounds, including chloro(phenyl)diacetylene[154]:

$$C_6H_5C{\equiv}CMgCl + ClC{\equiv}CCl \rightarrow MgCl_2 + C_6H_5C{\equiv}C{-}C{\equiv}CCl.$$

The reaction of ClC≡CR, in which R is an unsaturated radical, with organolithium compounds, gives highly unsaturated compounds, for example, diphenyloctatetrayne and *cis,cis*-deca-2,8-diene-4,6-diyne.

The haloacetylenes RC≡CX (mainly with X= Br) readily undergo the Arbuzov rearrangement under ordinary conditions with the formation of the esters of alk-1-ynylphosphonic acids:

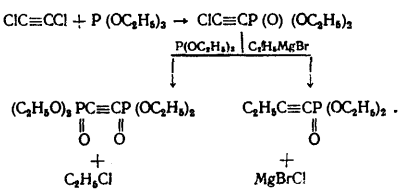
$$R'C{\equiv}CX + (RO)_3P \rightarrow R'C{\equiv}C{-}\underset{\underset{O}{\|}}{P}(OR)_2 + RX.$$

The yields are 67% for R′ = C_6H_5 and 48% for R′ = $-CH{=}CH_2$.[158] Analogous products were obtained also by the reaction of 1-bromoacetylenes with sodium dialkyl phosphites[133]:

$$(C_2H_5O)_2P(O)Na + BrC{\equiv}CR \rightarrow (C_2H_5O)_2P(O)C{\equiv}CR + NaBr$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_6H_5; yields 37–72%.

Ionin and Petrov showed[159] that dichloroacetylene also reacts readily with trialkyl phosphite. The chlorine atom in the diethyl chloroethynylphosphonate is labile. For example, it is replaced in the action of a second molecule of triphenylphosphine, organomagnesium compounds, etc.:



Di-iodoacetylene reacts with phenylhydrazine, exchanging one iodine atom by a phenyl radical[25]:

$$C_2I_2 + 2\,C_6H_5NHNH_2 \rightarrow C_6H_5NHNH_2 \cdot HI + N_2 + H_2 + C_6H_5C{\equiv}CI.$$

In reactions with organomagnesium compounds, both iodine atoms are exchanged by the residue MgX:

$$2\,RMgX + IC{\equiv}CI \rightarrow XMgC{\equiv}CMgX + 2\,RI.$$

Hence di-iodoacetylene can be used as an iodinating agent. The reaction is effected by simple addition of an ethereal solution of di-iodoacetylene to an ethereal solution of a Grignard compound with stirring at 0°C. The conversion proceeds without difficulty and with almost quantitative yield[86,97]. Therefore di-iodoacetylene is becoming a useful auxiliary medium for preparative organic chemistry. By this method, for example, iodobenzene is obtained from phenylmagnesium bromide and di-iodoacetylene in 95–97% yield. In a similar reaction phenylethynylmagnesium bromide with 2-iodo-1-phenylacetylene in the presence of cobalt(II) chloride gave diphenyldiacetylene with a yield of 75%. However, phenylethynylmagnesium bromide and di-iodoacetylene in this way did not give diphenyltriacetylene[160]. The reaction proceeds just as with other organomagnesium compounds:

$$2C_6H_5C{\equiv}CMgBr + IC{\equiv}CI \rightarrow 2\,C_6H_5C{\equiv}CI + BrMgC{\equiv}CMgBr.$$

Both iodine atoms in di-iodoacetylene can be replaced by hydrogen. Such exchange proceeds during reaction with potassium iodide in neutral or weakly acid aqueous solution:

$$IC{\equiv}CI + 2H_2O + 2\,KI \rightleftarrows H{-}C{\equiv}C{-}H + 2\,KOH + 2\,I_2.$$

C_2I_2 in alcoholic solution is also converted into acetylene under the action of zinc dust in dilute H_2SO_4 or by sodium amalgam. Also both iodine atoms are replaced by hydrogen in the electrochemical reduction of C_2I_2 at a mercury cathode. The reaction is[161]:

$$I{-}C{\equiv}C{-}I + 4e + 2\,H^+ \rightarrow H{-}C{\equiv}C{-}H + 2I^-.$$

The synthesis of bis(trimethylsilyl)acetylene by the reaction of tetrabromoethylene with trimethylchlorosilane and metallic magnesium in tetrahydrofuran[162] should be expected to lead to the conversions being considered, since the reaction undoubtedly proceeds through the intermediate formation of dibromoacetylene with subsequent replacement of both bromine atoms by the trimethylsilyl radical:

$$CBr_2{=}CBr_2 + 3\,Mg + 2\,(CH_3)_3SiCl \rightarrow 2\,MgBr_2 + MgCl_2 + (CH_3)_3SiC{\equiv}CSi(CH_3)_3.$$

Exchange of halogen atoms can be effected by the action of halogens on haloacetylenes. Information has been given above about the formation of hexachloro- and hexabromo-ethane from di-iodoacetylene. Ingold[69] observed the formation of di-iodoacetylene on passing chloroacetylene into a benzene solution of iodine. However, that conversion is accompanied by other reactions; therefore it has no preparative value.

4. Decomposition of the Haloacetylenes. Oxidations

Various authors[73,163,164] have observed the decomposition of di-iodoacetylene in light or on heating in solvents, proceeding by the equation:

$$2\,C_2I_2 = C_2I_4 + 2\,C.$$

Study of the kinetics in various solvents (benzene, chloroform, alcohol, etc.) at 100°C and 138°C showed that this is a first-order reaction. The mean temperature coefficient of its rate has been determined and it has also been found that the influence of the solvent on the rate constant is not great. The reaction is brought about by the violet part of the solar spectrum[80] and is catalysed by HgI_2.

The explosive decomposition of the haloacetylenes on heating without solvent proceeds with the release of carbon. Bromoacetylene and chloroacetylene decompose according to the equation[6,39]:

$$C_2HX \rightarrow HX + 2\,C$$

the dihaloacetylenes decompose to the elements. Bromoacetylene burns in air to give CO, CO_2, and HBr.[93] Lawrie[33] found that on oxidation in absolute alcohol by dry oxygen dibromoacetylene is 78.4% converted into C_2Br_4 by the reaction:

$$2C_2Br_2 + O_2 = C_2Br_4 + 2CO;$$

~15.6% of it is oxidised to oxalyl bromide, and ~6.1% forms ethyl dibromoacetate. Biltz[104] also found the formation of oxalyl bromide in the oxidation of C_2Br_2 by atmospheric oxygen, quoting this fact in support of the acetylenic structure of the substance. However, later work did not confirm Lawrie's results. Hauptmann writes that the oxidation of dibromoacetylene by oxygen in absolute alcohol either does not occur at all, or proceeds extremely slowly and does not go far. Straus and coworkers[163] assume that the reasons for the violent explosions of C_2Cl_2 and C_2Br_2 with traces of oxygen must be sought in the nature of the products of the addition of oxygen and not in the decomposition or oxidation itself. Other authors[71] state that the oxidation of chloroacetylene and bromoacetylene proceeds by a chain mechanism and the difference in the oxidation of acetylene and haloacetylenes C_2HX may be ascribed to the different relative stabilities of the intermediate peroxide compounds formed in the oxidation. Dichloroacetylene burns with the formation of carbonyl chloride[98].

In its careful oxidation, greatly diluted with carbon dioxide, CO and CO_2 are obtained, as well as carbonyl chloride, and the reaction can be expressed by the equation[35]:

$$2\,C_2Cl_2 + 5O \rightarrow 2\,COCl_2 + CO + CO_2.$$

A substance of general formula $(COCl)_x$ is formed simultaneously, which gives an anilide with aniline. However, its structure has not been found precisely. On passing oxygen into a 5–10% ethereal solution of dichloroacetylene the same substance was obtained as the main reaction products; formation of oxalyl chloride was not observed[34]. Di-iodoacetylene in neutral solutions is slowly oxidised in the air[42,43,73]:

$$2\,C_2I_2 + O_2 \rightarrow C_2I_4 + 2\,CO.$$

Ingold[69] oxidised chloroacetylene with hypochlorous acid and isolated chloroacetic acid, chloral hydrate, and dichloroacetaldehyde hydrate. The oxidation of di-iodoacetylene with cold conc. HNO_3 (d = 1.4) or chromic acid (in acetic acid) gives CO_2 and C_2I_4, but cold fuming HNO_3 gives CO_2, iodine, and tri-iodovinyl nitrate $I_2C{=}C(I)ONO_2$.[43]

5. Molecular Compounds of the Haloacetylenes

Such compounds are described for dichloroacetylene and di-iodoacetylene. Ott and Packendorff[35] found that with diethyl ether dichloroacetylene forms even under ordinary conditions a compound with b.p. 32.5°C at 743 mmHg. Ether depresses the autoxidation of dichloroacetylene and the compound does not ignite in a stream of pure oxygen, and also shows great resistance to bromine and ozone. It contains 62% C_2Cl_2, which corresponds to a molar ratio of the components, and decomposes water — in this, owing to the partial solubility of ether in water the dichloroacetylene released ignites. Ott[68] showed the importance of this compound: the C_2Cl_2 content in it is readily determined by volumetric analysis, and it allows various experiments with dichloroacetylene to be carried out without danger even in lectures. Recent investigators in working with dichloroacetylene have usually employed a solution of it in ether. Under other conditions the reaction of C_2Cl_2 with ether is more complex. In a boiling solution under the action of sunlight or ultraviolet radiation in the presence of catalysts (t-butyl peroxide, azo-bisisobutyronitrile) the reaction leads to the formation of several products, chiefly[150]:

$$CHCl{=}CClCH(CH)_3{-}O{-}C_2H_5 \text{ and } [CHCl{=}CClCH(CH_3)]_2O.$$

Analogous products (each in the form of *cis*- and *trans*-isomers) were obtained with chlorofluoroacetylene[18].

Other authors state that C_2Cl_2 reacts with ether at room temperature to form 1,2-dichloro-1-ethoxybut-1-ene and other similar compounds which have not been studied[27].

With secondary and tertiary amines di-iodoacetylene forms the compounds $(C_3H_7)_2NH.(C_2I_2)_2$, $(C_2H_5)_3N.(C_2I_2)_2$, and $C_5H_{11}N.(C_2I_2)_2$.[25] Furthermore, a compound of it with 1,4-dioxan is known[165], of composition $C_4H_8O_2.C_2I_2$.

Prévost states[166] that iodoacetylene forms various vinyl iodobenzoates with the complex $[(C_6H_5CO_2)_2Ag]^-I^+$. The same author observed an interesting reaction — the formation of C_2I_2 by the action of acetylene on the above complex — taking place, he thought, according to the equation:

$$2\,[(C_6H_5CO_2)_2\,Ag]^-I^+ + HC{\equiv}CH \rightarrow 2\,[(C_6H_5CO_2)_2Ag]^-H^+ + IC{\equiv}CI.$$

A reaction described by Nieuwland and Vogt[44,167] is also of interest. The authors showed that iodine is capable of replacing both hydrogen atoms in acetylene in a medium of liquid ammonia, and in this way C_2I_2 can be obtained in good yield:

$$C_2H_2 + 2I_2 + 2NH_3 \rightarrow C_2I_2 + 2\,NH_4I.$$

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THE MECHANISM OF THE FISCHER–TROPSCH REACTION AND THE INITIATED HYDROPOLYMERISATION OF ALKENES, FROM RADIOCHEMICAL AND KINETIC DATA

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I. INTRODUCTION

In the last ten years, the mechanism of the formation of hydrocarbons and their derivatives from CO and H_2 by the Fischer–Tropsch process has been discussed[1-4] in connection with the mechanism of the hydropolymerisation of alkenes under the influence of small quantities of CO in the presence of H_2.[5,6] This relates chiefly to processes on Co catalysts, since it is only on these catalysts that the hydropolymerisation of alkenes takes place[7-9]. This group of reactions based on CO is of general interest for the theory of heterogeneous catalysis, since in this field data have been obtained indicating the existence of planar chains and also the important part played by intermediate surface compounds of the radical type in various heterogeneous catalytic reactions. It is therefore convenient to combine the examination of the mechanism of the hydropolymerisation of alkenes with a discussion of new data on the mechanism of the Fischer–Tropsch reaction, particularly since they are associated with a number of common unresolved or partially resolved theoretical problems.

Among the fundamental more or less completely solved problems in the mechanism of the Fischer–Tropsch reaction we can include first of all the carbide hypothesis[10] and the Rideal–Craxford neocarbide theory[11-13], according to which bulk carbides or surface carbides respectively, formed from CO and the metal of the catalyst, are intermediate products. These views were subjected to well-founded criticism as early as the nineteen forties[14-18]. Of the later data refuting these hypotheses, we may mention the results of work by Roginskii and coworkers[19] on the exchange of carbides, labelled with ^{14}C, with carbon monoxide on a Co catalyst and of work by Indian authors[20], who showed that under the normal conditions of the preparation of hydrocarbons on a Co catalyst, the CO is present on the surface chiefly as the chemisorbed gas and is not fixed to any significant extent in the form of carbides; a single treatment in a vacuum at 200° removes the CO from three-quarters of the surface.

Another hypothesis which has been refuted is the theory[11-13] of a "giant" molecule, formed by the polymerisation of methylene radicals and undergoing hydro-cracking under the influence of atomic hydrogen to give the final products. The justified[21] rejection of this hypothesis, however, had to some extent an undesirable effect, since it led to an underestimation of the part played by degradation processes in the reaction and the part played by hydrocarbon radicals in the formation of the chains.

The most important, continuously discussed theoretical problems related to the mechanism of the two reactions being considered are: (1) the part played by oxygen compounds as intermediate products; (2) the part played by heterogeneous hydrocarbon and oxygen-containing radicals at the start of chain formation and in the process of chain growth; (3) the chemistry of the formation of C–C bonds between the units of the chains — the choice between polymerisation and condensation schemes, and (4) the part played by degradation processes in the formation of the final reaction products.

II. THE THEORY OF INTERMEDIATE FORMATION OF ALCOHOLS IN THE FISCHER–TROPSCH REACTION

The theories of intermediate alcohol formation in the Fischer–Tropsch reaction are held chiefly by American (Storch and Emmett) and English (Gibson) workers, who have made extensive studies of the reactions of alcohols under the conditions of the preparation of hydrocarbons from CO and H_2. Since it was initially assumed[22] that methanol is formed from CO and H_2 on the catalyst surface, the transformations of this alcohol were studied first. The starting point was provided by the results of our work[23], according to which the rate of formation of hydrocarbons from methanol in the presence of a catalyst consisting of $Co-ThO_2$ on kieselguhr at 200° is less than that for the reaction from CO and H_2, so that the formation of hydrocarbons from this alcohol is preceded by its decomposition to CO and $2H_2$. These results, in the opinion of Storch and coworkers[24], do not necessarily indicate that the methanol decomposes; the authors considered it possible that a primary complex is formed from the alcohol on the catalyst. Shortly afterwards, Kummer and Emmett[25] reached the same conclusion with reference to the transformation of methanol on an Fe catalyst, on the basis of their radiochemical studies. Our results were confirmed, however, by Gibson and coworkers[26], who pointed out that the primary reaction in the presence of a Co catalyst is the decomposition of methanol to CO and $2H_2$, from which the hydrocarbons are formed in a secondary reaction. These contradictions led Darby and Kemball[27] to make a detailed study of the transformation of methanol on a $100Co : 6ThO_2 : 3MgO : 200$ kieselguhr catalyst at various points along the catalyst layer. It was found that at 192° methanol reacted to the extent of 53%, of which only 1% was converted into reaction products. Analogous results were obtained over a wide range of temperatures (163–210°). The reaction was of first order with respect to alcohol, the reaction rate was decreased by carbon monoxide, and when allowance was made for the side reaction of methane formation from CO and H_2, it was found that the addition of H_2 has little influence on the kinetics, which is given by the equation:

$$-\frac{dp_{CH_3OH}}{dt} = k\frac{p_{CH_3OH}}{1+bp_{CO}}.$$

Hydrogen is adsorbed less strongly than methanol; its adsorption possibly takes place on different centres. The rate-limiting stage of the process might be the adsorption of the alcohol, which takes place less extensively than the adsorption of CO, or the decomposition of the adsorbed methanol. It was concluded that methanol is not converted directly into the reaction products but undergoes preliminary decomposition to CO and H_2, in agreement with published results[23,26].

On the basis of data on the transformations of methanol, ethanol, and formic acid on a Co–ThO_2–kieselguhr catalyst, Eidus[23] suggested that when the catalytic reduction of CO by hydrogen is incomplete, the formation of the methylene radical is preceded by the formation of an oxymethylene radical on the surface. It was later shown[28] that a CH_2O complex is formed during the successive adsorption of CO and H_2 on a catalyst of this type. The fact that methanol is not converted directly into hydrocarbons on a Co catalyst was attributed[27] to the fact that the methanol adsorption complex, inactive in the hydrocarbon synthesis, is isomeric with the active oxymethylene and is slowly converted into the latter; this explains the too low concentration of oxymethylene radicals formed from methanol:



Taking into account published data[29], it was concluded[27] that the reaction of methanol takes place in different ways on Co and Fe catalysts. Emmett and coworkers[30] found that when 1.4% methanol labelled with ^{14}C is added to the original $CO : H_2$ mixture in the presence of an Fe catalyst at 240° and 1–7.8 atm, the growth of the hydrocarbon chains can begin with the alcohol; the alcohol can take part to a slight extent in chain growth. Analogous results were obtained with formaldehyde, which, however, decomposes rapidly and completely on the catalyst surface with the formation of CO and CO_2, whose radioactivity is equal to that of the original formaldehyde. The molar radioactivity of the final reaction products increases linearly with increase in the number of carbon atoms in the molecule (the C number). The addition of 1.4% CO_2, labelled with ^{14}C, to the original mixture of CO and H_2 showed that at atmospheric pressure, other conditions being equal, CO_2 undergoes little conversion into CO or hydrocarbons, evidently due to the low rate of reaction of water gas. It was concluded[30] that neither methanol nor formaldehyde, on adsorption, form a complex identical to the primary complex from which growth of the carbon chain begins in the preparation of hydrocarbons from CO and H_2.

Evidence put forward in support of the intermediate formation of alcohols in the preparation of compounds from CO and H_2 includes the similarity in the structures of the alcohols and hydrocarbons in the Synthol process on an Fe catalyst (p. 474 of Ref. 24) and also the similarity in the curves giving the distribution of the branched alcohols and hydrocarbons formed on this catalyst with respect to C number[31]. Weitkamp[31] considers that the formation of alcohols and hydrocarbons on Fe catalysts takes place by a single mechanism with the primary formation of both alcohols and alkenes, and also that the alcohols do not undergo dehydration and are not precursors of the alkenes.

Studies on the correlation of the rates of decomposition of alcohols in mixtures with CO and H_2 with the rates of their formation from CO and H_2 on Co catalysts were carried out by Gibson and coworkers[26,32,33]. Under the usual conditions of preparation (190°, 10 atm) from a $CO : 2H_2$ mixture on a standard catalyst ($100Co : 5ThO_2 : 8MgO$: 200 kieselguhr), the final product contains only 1% of alcohols and aliphatic acids. If, however, the reaction temperature is lowered and the duration of contact decreased, the concentration of normal primary alcohols may increase to 60%. These results are also taken as evidence for the intermediate formation of alcohols. The alcohol-enriched reaction product obtained at 10 atm and 160–170° from a 37.5 g m^{-3} $CO : 2H_2$ mixture with a degree of conversion equal to 10–20% was studied[26] to determine the distribution of the alcohols with respect to C number. The distribution was compared with the relative stability of the normal primary alcohols under the conditions of preparation in a mixture with H_2 or $CO + H_2$. It was concluded that ethanol and higher primary alcohols are converted directly into hydrocarbon products without intermediate decomposition with the formation of CO. Slightly different results were obtained[23] for ethanol, which decomposes on a Co–ThO_2–kieselguhr catalyst at 200° with the formation of a gas with composition: 48.3% H_2, 27.7% CH_4, 9.6% CO, 9.0% C_2H_6, 2.9% unsaturated hydrocarbons, and 2.5% CO_2. It was assumed that the initial product is acetaldehyde, which subsequently decomposes to CH_4 and CO. Hydrocarbons are formed in 6% yield in a secondary reaction from CO and H_2. According to Gibson's data[32], ethanol was found to be the most stable of the alcohols studied under the reaction conditions; at 150° it is converted into saturated gaseous hydrocarbons and water; at 185° it forms gases, containing 9% CO, and liquid hydrocarbons, whose yield, however, was 21% greater (relative to the ethanol used up in the reaction) than could have been obtained in the normal preparation from CO and H_2. The alcohol is apparently dehydrated to form ethylene, which reacts with CO and H_2, undergoing hydropolymerisation[5,6]. Homologues of ethanol decomposed in the mixture with $CO + H_2$ at 150° at a rate comparable with the rate of preparation from CO and H_2. The chief reaction was dehydration. In accordance with its stability, ethanol was obtained in the preparation from CO and H_2 in relatively high yields: 8.6% of the total liquid products and more than 50% of the total alcohols in the aqueous layer. Decrease in the temperature of the reaction and increase in the pressure and volume rate of the original gas led to a decrease in the rate of decomposition of the alcohols and a simultaneous increase in their concentration in the product of the preparation from CO and H_2. The yield of alcohols also increased with decrease in the degree of conversion of the original mixture and increase in the $CO : H_2$ ratio in this mixture. Decrease in the temperature of the reaction and in the $CO : H_2$ ratio, and increase in the degree of conversion of CO and in the activity of the catalyst led to an increase in the average molecular weight of the final product. At a low degree of conversion of about 20–30%, increase in pressure from 1 atm to 11 atm led to a decrease in the average molecular weight, whereas at degrees of conversion greater than 50% an increase in the average molecular weight was observed[33]. The alcohols are not formed from alkenes by an oxo-synthesis scheme via the aldehydes, but are most probably formed directly from CO and H_2 by a mechanism involving the stepwise growth of the carbon chain on the catalyst[34–38]. The most probable process[32] is the stepwise attachment of methylene radicals to the end of the growing chain, which terminates in an oxymethylene group[23]. The chains are desorbed by hydrogen with the formation of saturated alcohols. If the desorption does not depend on the C number and a definite fraction (α) of chains with any C number are desorbed before further growth, the curve giving the distribution with respect to C number for the alcohols formed at the start of the reaction is given by the formula

$$Y_n = K \cdot \alpha (1-\alpha)^{n-1},$$

where Y_n is the molar quantity of alcohol with C number equal to n, and K a constant. With a correction for stability, the calculated curve coincides with the experimental curve, the maximum corresponding to ethanol, in agreement with the experimental data.

Comparison of the curves giving the distribution of the alcohols with respect to C number with the distribution

curve for the hydrocarbons obtained on a Co catalyst by Martin[39] under ordinary conditions shows some discrepancies. The curve giving the yield of hydrocarbons, unlike the curve giving the yield of alcohols, which shows a maximum at C_2 in the range C_2–C_5, showed a minimum. This difference might be contradictory to the theory of intermediate alcohol formation. It was suggested that in the preparation, ethanol undergoes dehydration to ethylene, which subsequently undergoes hydrocondensation with CO[40] and hydropolymerisation[5,6]. Since the rates of these reactions decrease on going from ethylene to propene and butene[41,42], the maximum on the curve should be displaced towards C_5. It is not excluded that ethanol reacts with CO and H_2 without decomposition, as is the case on an Fe catalyst[25,29].

The results of the correlation of the rates of formation and decomposition of the alcohols and the influence of the process conditions on these rates were taken[32,33] as confirming the theory of intermediate alcohol formation, although it is possible that alkenes are also primary products. The reaction mechanism changes to some extent with change in the conditions: if these are favourable for the preparation of hydrocarbons, the formation of the chains involves methylene radicals, into which the oxymethylene radicals, which are unstable under these conditions, are converted; if, however, the conditions are favourable for the preparation of alcohols, there is an increase in the stability and concentration of the oxymethylene radicals, and these play a predominant part in the growth of the chains. It is possible that a decrease in the length of the carbon chains takes place as a result of secondary hydro-cracking reactions.

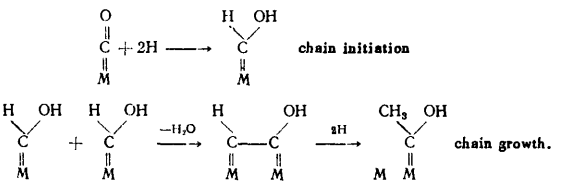
In Gibson's opinion[32], the results of Eidus and coworkers[5] indicate that the growth of the hydrocarbon chains begins only in the presence of radicals containing oxygen, since ethylene and hydrogen are converted into into ethane, and the addition of less than 1% CO leads to the formation of higher hydrocarbons. The appreciable yields of hydrocarbons with odd C number indicates dissociation of the ethylene molecule into two methylene radicals.

III. START OF FORMATION AND GROWTH OF CARBON CHAINS

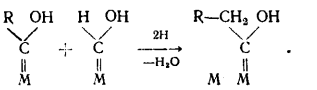
1. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Alcohols

Important radiochemical studies on the mechanism of the Fischer–Tropsch reaction were carried out by Emmett and coworkers, who studied the reactions of the original gaseous mixtures with added alcohols labelled with ^{14}C. The reaction was first carried out on an Fe catalyst promoted with Al, Zn, and Th oxides, at atmospheric pressure and 230° with a $1CO : 1H_2$ gas mixture containing 1.6 vol.% ethanol labelled with ^{14}C in the methyl or methylene group. It was found that the molar radioactivity of the methane was negligible, that of the C_5–C_{10} hydrocarbon fraction appreciable and independent of the C number, and that of the C_2–C_4 fractions slightly less than that of the liquid hydrocarbons. These results show that ethanol does not decompose before taking part in chain growth and that its adsorption complex plays the part of intermediate product in the preparation. The radioactivity of the C_2 fraction indicates successive dehydration and hydrogenation of the alcohol. Experiments on the stepwise splitting of the propane molecule showed that ~90% of the attached C atoms combine with the α-C atom of the adsorbed alcohol complex and only ~10% with the β-C atom.

Experiments under the same conditions with the addition of 1.5% labelled propanol or isobutyl alcohol to the original gas gave C_2–C_{10}, C_3–C_{10}, and C_4–C_{10} fractions which had an almost constant molar radioactivity, equal to between one-third and one-half the radioactivity of the original alcohol. Isopropyl alcohol underwent intensive conversion into isobutane and isobutene. Only one C_7 molecule out of 15 and one C_9 molecule out of 27 were formed with the participation of labelled isopropyl alcohol. t-Butyl alcohol apparently did not take part in the formation of hydrocarbons under these conditions. Experiments with labelled propanol gave n-butane containing ^{14}C, and isobutane containing no ^{14}C. In experiments with labelled isopropyl alcohol, on the other hand, the isobutane was radioactive and the butane was not. Adsorbed methanol also took part in the formation of carbon chains, but with an efficiency which was only one-quarter of that for the other alcohols used. These results led to the conclusion that in the Fischer–Tropsch synthesis on Fe catalysts the CO and H_2 form primary complexes similar to the adsorbed complexes of primary alcohols. Kummer and Emmett[29] put forward a scheme for the growth of the carbon chains, similar to the schemes advanced by others[31,35,38]. In this scheme the chief part in the formation of the carbon chains is played by the CHOH radical. This takes part in the formation of C–C bonds by condensation with the liberation of water from the hydroxyl of one oxymethylene group and the hydrogen of another:



In general:



Chain termination takes place by desorption of aldehydes, hydrogenation to alcohols, decomposition to alkenes, etc.

Subsequent experiments with the addition of labelled ethanol[43,44] showed that it is included in the reaction products more intensively in the preparation on a once-promoted Fe catalyst than on a twice-promoted catalyst, and more intensively on a catalyst which had not been treated with nitrogen than on a catalyst treated with nitrogen. The radioactivity of the reaction products decreased with increase in pressure in the range 1–21 atm. The radioactivity of the alcohols formed on a catalyst treated with nitrogen was approximately the same as that of the hydrocarbons in the range of C numbers C_3–C_6. With the addition of 0.04 vol.% strongly radioactive ethanol, it was shown that the increase in the extent to which the alcohol is included is slower than the increase in the partial pressure of alcohol in the original gas.

In experiments with an Fe catalyst at 224°, with the addition of 1.5% propanol or propanal to the original gas, almost half of the final products were formed with the participation of these compounds; the butane and butenes had the normal structure.

Soviet workers [45] published the results of experiments on the preparation on a 100Co : 18ThO_2 : 100 kieselguhr catalyst with a CO : 2H_2 mixture containing added labelled ethanol at 195°. The molar radioactivity of the C_6–C_{29} hydrocarbons was constant and independent of the C number. An average of one molecule out of 18 was formed with the participation of the alcohol. The molar radioactivity of the methane and C_2–C_4 hydrocarbons was slightly less than the molar radioactivity of the liquid hydrocarbons. In analogous experiments by American workers [43], one hydrocarbon molecule out of 60 was formed with the participation of labelled ethanol with the same concentration in the original gas, that is, the quantity was much less than that in the presence of any Fe catalyst. The methane had approximately the same radioactivity as the higher hydrocarbons, whereas on Fe catalysts it had a radioactivity which was 10–100 times less than that of the higher hydrocarbons. In the product of the reaction with a Co catalyst, the greatest molar radioactivity was shown by the C_2 fraction; this was attributed to the fact that the species included in the chain was not ethanol, but its dehydration product, ethylene, which undergoes partial hydrogenation to form ethane. When 1.5% ethanol is added, it is included in the chain to a greater extent than when 0.04% is added, but the increase is less than the increase in the concentration. Emmett and coworkers [43] concluded that on Fe catalysts, alcohols are intermediate products in the preparation of hydrocarbons from CO and H_2, but that the mechanism of the preparation on Co catalysts differs from that on Fe catalysts.

Soviet workers [45] consider that these and other data [25,29] indicate that transfer of the chain, which begins with the adsorption of alcohol molecules, produces material chains with a number of units up to n - 1, where n is the C number of the hydrocarbons. The observed coefficient 1 : 18 may express the ratio of the units in the reaction and material chains. Thus one unit in the reaction chain corresponds to one material chain. The fact that the molar radioactivity of the liquid hydrocarbons is constant with change in C number reflects the single mechanism of chain formation with the direct participation of the labelled alcohol or its adsorption complex. This participation, however, may be manifested not only in the initiation of chain growth, as assumed by Emmett and coworkers [25,29], but also in the termination of the material chains, which leads to the same results. The Soviet workers [45] point out that neither their results nor the results of Emmett and coworkers [25,29] provide a basis for rejecting the methylene-polymerisation scheme, since it has not been proved that CH_2 radicals cannot take part in chain growth initiated by alcohol. A parallel reaction without inclusion of alcohol also does not exclude the participation of CH_2 radicals. Moreover, a stage involving the polymerisation of CH_2 radicals on a Co catalyst is confirmed by the hydropolymerisation of alkenes [5,6]. The oxymethylene-condensation scheme for the formation of carbon chains is more probable for the mechanism of the iso-synthesis in the presence of oxide catalysts, in view of the semi-contact character of the hydrogenation of CO under these conditions [46].

The fact that the adsorption complexes of alcohols tend to bring about the growth of carbon chains in the presence of CO and H_2 on Co and Fe catalysts still does not prove that the true primary complex formed from CO and H_2 is an alcohol-like product. It was therefore of interest to add compounds of other classes to the original gas.

Experiments on a Co catalyst were carried out with gas containing added acetaldehyde or ethanol labelled with ^{14}C in both carbon atoms, and with methyl formate labelled in the methoxycarbonyl group [47]. The products of the reaction with ethanol and acetaldehyde showed a constant molar radioactivity with increase in C number, whereas the products of the reaction with methyl formate showed a linear increase in the molar radioactivity with increase in C number, the molar radioactivity in the first two reactions amounting to 5–6%, and that in the last reaction to 63% of the radioactivity of the original labelled compound. This shows that methyl formate, like formic acid [23], decomposes on the catalyst surface with the formation of CO, which, however, reacts at the moment of formation, since the radioactivity of carbon monoxide in the gas is low. The similarity in the results of the experiments with ethanol and acetaldehyde indicates that the aldehyde is reduced to the alcohol. Chain growth is due to an adsorption complex of alcohol, but it has not been proved that it contains oxygen.

2. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Alkenes

Experiments carried out at 195° on a Co catalyst with an original mixture of CO and H_2 containing ethylene labelled with ^{14}C are of particular interest in the investigation of the mechanism of the hydropolymerisation of alkenes [5,6]. Under these conditions, ethylene is converted into higher hydrocarbons to the extent of 25% and into ethane to the extent of 50%. The molar radioactivity of the liquid hydrocarbons remained constant with change in C number and at concentrations of ethylene in the original gas equal to 0.78% and 1.48% it amounted to 10% or 22% respectively of the radioactivity of the added ethylene. Thus under these conditions the extent to which the labelled compound took part in chain formation increased in proportion to its concentration. The results obtained show that ethylene is present in the primary complex bringing about the growth of the material chains on the catalyst. Chain termination by ethylene must be excluded, since increase in its concentration in the original gas does not lead to a decrease in the yields of the higher hydrocarbons. The hydropolymerisation of ethylene [5,6] also provides evidence against chain termination by ethylene.

Comparison of published data [45,47,48] indicates that ethylene takes part to a greater extent than ethanol in the formation of hydrocarbons on a Co catalyst. One molecule out of 4–5 is formed with the participation of the labelled compound when using ethylene, compared with the figure of one molecule out of 18 for ethanol. It is possible that the alcohol is first dehydrated to form ethylene, which then enters the complex initiating chain growth. This casts doubt on the applicability of the condensation scheme. All these facts taken together leave no doubt that the growth of hydrocarbon molecules on the catalyst surface takes place by a chain mechanism.

Experiments [19] on a Co catalyst at 195° with an original mixture containing 1.5% labelled propene showed that the molar radioactivity of the liquid products remained constant with change in the C number, but that propene took part in the formation of products to a smaller extent than ethylene: only one out of 12 hydrocarbon molecules was produced with its participation. The lower reactivity of propene compared with ethylene was previously observed in hydropolymerisation under the influence of CO. [41,49] An interesting feature is that increase in the concentration of labelled alkene in the original mixture of CO and H_2 above a definite limit may lead not only to participation of the alkene in the

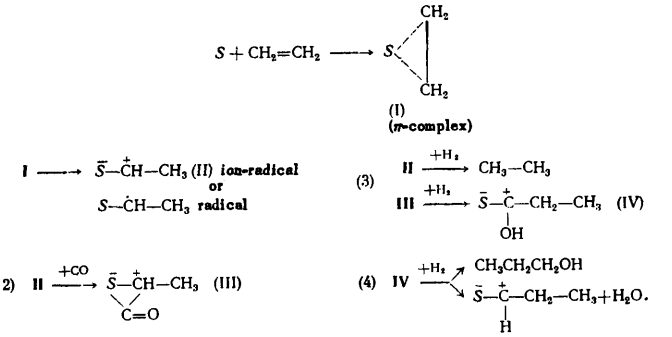
formation of the primary complex, but also to its participation in chain growth. This was observed[19] by the addition of 4.8% ethylene, when the molar radioactivity remained unchanged with change in the C number of the hydrocarbons in the range 5–9, but increased for hydrocarbons above C_9. This phenomenon can be regarded as an intermediate stage between the Fischer–Tropsch reaction and the hydropolymerisation of the alkene. Under these conditions one out of 1–2 molecules of C_5–C_9 hydrocarbons was formed with the participation of the labelled carbon of ethylene.

In the reaction on an Fe catalyst at 224° with a $CO:H_2$ mixture containing 1.25% labelled ethylene, the quantities of hydrocarbons formed with its participation amounted to 12% at 1 atm and 6% at 6.5 atm. These results show that ethylene may initiate chain growth, but not to the same extent as primary alcohols[44].

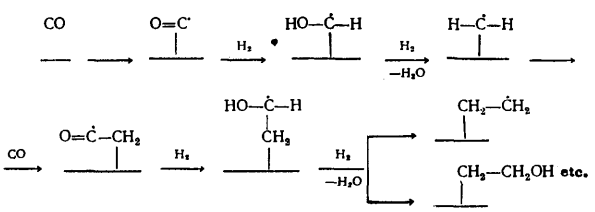
A very interesting series of studies has been carried out by Kryukov, Bashkirov, Kagan, and their coworkers on the mechanism of the preparation of alcohols and hydrocarbons on fused Fe catalysts at 160–300° and 20–150 atm at a volume rate of gas equal to 500–2000 h^{-1}, using the tracer method[50–55].

Under these conditions, butanol labelled with ^{14}C and added in quantities of 0.04–0.1% to an original $1CO:2H_2$ mixture remained 90–95% unchanged. Less than a hundredth of the resulting hydrocarbons above C_4 and of C_6–C_9 alcohols could have been formed with its participation[51]. Thus butanol is not an intermediate product of the preparation. The slight radioactivity of the pentanol and hexanol formed, however, indicated the formation of a radioactive complex containing oxygen. Labelled butene added to the original gas (90 atm and 220°) underwent hydrogenation, oxidation, and hydro-cracking, took part to some extent in the formation of C_5 products, but took no part in the formation of alcohols and hydrocarbons above C_9.[52] As expected, methanol was less stable than butanol under these conditions and underwent various transformations, particularly decomposition to CO and H_2.[51] It took part not only in chain formation, but also in chain growth, as indicated by the increase in the molar radioactivity of the product with increase in the C number. The fact that the radioactivities of alcohols and hydrocarbons with equal C numbers were the same was attributed to their formation from the same "precursor", that is, from the same primary complex, formed from CO and H_2 and containing oxygen in addition to carbon and hydrogen[50,51]. The primary complex bringing about growth of the carbon chain is formed by the reaction of CO, activated on an Fe atom dissolved in iron carbide, with hydrogen, physically adsorbed on neighbouring carbide atoms[54]. An interesting feature is that in the study of the part played by iron carbides using CO labelled with ^{14}C in experiments on fused catalysts (300° and 20 atm) it was found[53] that in this instance they cannot be regarded as intermediate products. The carbides were hydrogenated to form methane and exchanged carbon with CO. Both of these processes took place very slowly. Only one out of 3000 CO molecules underwent exchange and five out of 3000 CH_4 molecules were formed from the labelled carbide. Hydrocarbons could have been formed via the carbides to the extent of only 0.03%. Even from this low degree of conversion of carbides into reaction products it is possible to estimate the part played by methylene radicals in chain formation. On the basis of data obtained in a study of ethylene added to the original gas and iron carbides labelled with ^{14}C, it was concluded[55] that the chains may grow simultaneously in two main ways: by condensation of intermediate oxygen-containing compounds with the liberation of water, and by polymerisation of surface compounds which may or may not contain oxygen. In the polymerisation scheme, growth of the carbon chain takes place at the end of the molecule which does not contain the hydroxyl group. An analogous dual mechanism for the growth of carbon chains in the iso-synthesis[56–59] was proposed by Eidus[46]. A slight difference was that Eidus[46] assumed stepwise growth not only by groups containing one C atom but also groups containing several C atoms. Some of the stages in the two schemes, particularly in the initial stages, are similar or even identical.

To explain the participation of ethylene in chain initiation, Roginskii and coworkers[19] proposed a step scheme in which ethylene, after formation of a π-complex with the catalyst and conversion into an ion-radical or ethylidene radical, combines with an adsorbed CO molecule, forming successively, and with the participation of hydrogen, ion-radicals or α-hydroxypropylidene radicals and then α-propylidene, with regeneration of the unsaturated carbon atom in the α-position to the catalyst:



Voevodskii and coworkers[60] put forward a chain scheme for the preparation of organic compounds from CO and H_2, involving the gradual growth of a univalent surface radical:

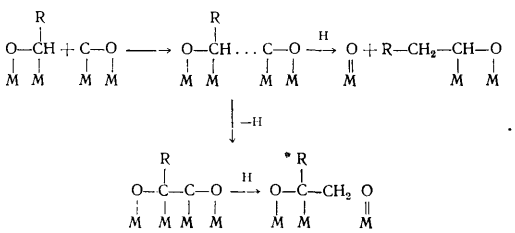


3. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Keten

Blyholder and Emmett[61] used keten labelled with radioactive ^{14}C in the methylene group. The experiments were carried out on an Fe catalyst at atmospheric pressure and 247° with the addition of 2% keten to a $CO:H_2$ mixture. The hydrocarbon product had an almost constant molar radioactivity, which was independent of the C number and equal to the radioactivity of the original keten. Analogous experiments were made with the addition of 0.25% labelled keten to a $1CO:2H_2$ mixture (Co–ThO_2–MgO–kieselguhr catalyst) at 185°. The molar radioactivity of the hydrocarbons was approximately independent of the C number and amounted to one-third of the radioactivity of the keten. The methane formed was not radioactive. Since the adsorbed keten

underwent intensive introduction into the reaction products, it was concluded that its adsorption complex is similar to the primary complex of the Fischer–Tropsch reaction. It was assumed that the keten molecule is joined to the catalyst surface by metal–carbon and metal–oxygen bonds. The following three possible results from the introduction into the reaction of a keten labelled in the methylene group were examined: (1) for dissociation of the keten into methylene and CO, assuming the applicability of the methylene–polymerisation scheme, the reaction product should have a molar radioactivity directly proportional to the C number; (2) with dissociation of the keten into CH_2 and CO, if polymerisation of the methylene radicals or their inclusion in the preparation by another mechanism do not take place, the reaction product should not be radioactive, whereas the methane should be radioactive; and (3) if the keten does not dissociate, but initiates chain growth, the reaction product should have a radioactivity which is independent of the C number. The experimental data appear to confirm the third possibility.

The results obtained show that on Co and Fe catalysts the keten is converted almost completely into reaction products, indicating that it is strongly adsorbed and possibly that an oxygen–catalyst bond is formed. The possibility of formation of such a bond is indicated[62] by the exchange of O atoms between $^{12}C^{16}O$ and $^{13}C^{18}O$ on an Fe catalyst, which shows that the CO is joined to the surface through the C and O atoms. In accordance with this, Blyholder and Emmett[61] proposed a reaction scheme in which the keten and CO are adsorbed through the C and O atoms, and new C–C bonds are produced between the carbon of the carbon monoxide and the carbon of the carbonyl group of the keten without condensation with the liberation of water. Oxygen is liberated in the form of atoms adsorbed on the catalyst:



The keten is adsorbed more strongly than saturated alcohols, so that it is more effective at the start of chain growth. According to Blyholder and Emmett[61], alcohols should undergo preliminary dehydration before forming the initial complex. This is indicated by the ability of ethylene to form a complex which brings about chain growth. Ethane does not exhibit these properties.

Blyholder and Emmett[61] considered three possible results of the use of keten, but they did not consider the fourth, most probable possibility: dissociation of the keten with the subsequent participation of the methylene radical in chain initiation. New conclusions were reached in subsequent work[63]. The reaction was carried out on a once-promoted Fe catalyst at 256° with the addition of 0.7% keten, labelled in the carbonyl group, to the original gas, and on a Co catalyst at 189° with the addition of 0.5% of the same keten. Hydrocarbons with molar radioactivity directly proportional to the C number were formed on both catalysts. Thus the keten undergoes preliminary dissociation on the catalyst with the formation of a methylene radical, which initiates the chain, and carbon monoxide, which takes continuous part in the chain growth. The exchange of carbon between CO and the keten under these conditions is slight and is not reflected in the results. Convincing confirmation was thus obtained for the initiation by heterogeneous methylene radicals of the growth of chains in the Fischer–Tropsch synthesis on Co and Fe catalysts. This shows that not only oxygen-containing but also hydrocarbon radicals exhibit these properties. The results obtained, however, did not touch on the polymerisation of CH_2 radicals. It would be of interest to use higher concentrations of keten, labelled in the methylene group, to study this process. The CH_2 radicals would then take part in chain growth in a fashion analogous to that of ethylene at higher concentrations[19]. An interesting feature is that the addition of 0.5–0.7% keten to the original gas led to an increase in the yield of lighter products.

4. Radiochemical Studies of the Hydropolymerisation of Ethylene Using Labelled CO

Gibson and Fletcher[64] described a study of the mechanism of the hydropolymerisation of ethylene under the influence of CO. The chief aim of this work was to investigate the part played by two types of radical: hydrocarbon radicals and oxygen-containing radicals. It was assumed that an oxygen-containing radical initiates chain growth, since hydropolymerisation does not take place in the absence of CO but takes place to an appreciable extent at a concentration of 0.1% CO in the original gas[5]. The reaction was carried out on a $100Co : 5ThO_2 : 8MgO : 200$ kieselguhr catalyst at 185° with a $C_2H_4 : H_2$ mixture containing 5% CO labelled with ^{14}C. 50–60% of the CO and almost all the ethylene, 50% of which was hydrogenated to form ethane, took part in the reaction. The molar radioactivity of the C_4–C_{10} hydrocarbons increased regularly with increase in the C number. Approximately one out of 6–7 carbon atoms was produced from CO. The molar radioactivities of the methane and ethane were low. Side-products of the Fischer–Tropsch reaction were formed in small quantities. With the exception of appreciable yields of C_4 hydrocarbons, the formation of large quantities of other true polymeric forms was not observed. Gibson and Fletcher[64] consider that this confirms the earlier conclusion (see p. 341) that ethylene dissociates into two methylene radicals, forming hydrocarbons and methane. Comparison of the radioactivity of the hydrocarbons with the radioactivity of the original CO shows that some of the molecules formed do not contain C atoms originating from the CO. This means that after initiation of the reaction, chain growth can continue and be renewed to some extent without the participation of CO. Gibson and Fletcher[64] quote the results of Eidus and coworkers[65], according to which, after the reaction of a mixture of CO, H_2, and C_2H_4, it is possible to obtain liquid hydrocarbons for some time by passing a mixture of C_2H_4 and H_2 containing no CO over the Co catalyst. These experiments were repeated[66] using ^{14}CO; the same results were obtained, and both the volatile and high-boiling fractions of the reaction product contained ^{14}C. These data[64,65] show that the formation of hydrocarbon chains is also possible even when the original C_2H_4–H_2 mixture does not contain CO. Chain growth is initiated by radicals on the catalyst surface, for which CO is necessary at the start of the reaction. These heterogeneous radicals can apparently be subsequently regenerated from ethylene even in the absence of CO. This explains the absence of ^{14}C in a fraction of the reaction products, and their formation from a mixture of C_2H_4 and H_2.

Determination of the radioactivities of each of the three C atoms in the molecule of the propene liberated[64] gave the following radioactivity ratio:

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3}$$
$$304 : 26.5 : 220 .$$

The low radioactivity of the central C atom shows that it comes chiefly from the ethylene. The radioactivity may provide a measure of the quantity of propene formed by the Fischer–Tropsch reaction from CO and H_2. If the propene were formed by the direct attachment of a C atom from CO to an ethylene molecule by hydrocondensation[40,67,68], one of the terminal C atoms should show a high radioactivity. The high radioactivity of both terminal C atoms is apparently due to migration of the double bond, which takes place readily on a Co catalyst; this has been shown many times[69-76]. The propene formed from CO and H_2 then exhibits radioactivity:

$$CH_2=CH-CH_3$$
$$26.5 : 26.5 : 26.5.$$

The initial distribution of the radioactivity in the propene formed by the hydropolymerisation of ethylene is as follows:

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3}$$
$$471 : 0 : 0 .$$

A study was made[77] of the distribution of the radioactivity in propanol, whose yield amounted to 4% of the liquid products of the reaction. The propanol was converted into propene by a method which prevented movement of the double bond. The following radioactivity distribution was observed:

$$\underset{15}{\overset{3}{CH_3}-\overset{2}{CH_2}}-\overset{1}{CH_2OH}$$
$$85$$

The molar radioactivity of the propanol was 11 times the radioactivity of the propane and more than one-third of the radioactivity of the original carbon monoxide. All the propanol was formed according to the reaction

$$CH_2=CH_2 + {}^{14}CO \longrightarrow CH_3CH_2{}^{14}CH_2OH.$$

Less than 10% of the C_3 products was formed with the participation of ^{14}CO, and the greater part was formed from the carbon of the ethylene. It was therefore concluded that the ethylene dissociates into two methylene radicals. The distribution of the radioactivity is of the same type for propene and propanol, as a result of the fact that the ^{14}C is attached to the ethylene in the form of CH_2 or oxygen-containing radicals with one ^{14}C atom in each instance; it is possible that propene is formed from propanol. Since the original gas contains a large quantity of ethylene, the hydropolymerisation is not identical with the Fischer–Tropsch reaction, but the fact that the radioactivity distribution is the same for propanol and propene was taken[77] as confirming the previous suggestion that in the Fischer–Tropsch reaction on a Co catalyst the primary products are alcohols, from which alkenes and alkanes are produced by dehydration and hydrogenation.

The characteristics of the liquid product of the hydropolymerisation of ethylene, obtained from an equimolar mixture of ethylene and hydrogen containing ~5% CO are given in the Table. The slight discrepancies in the data must be attributed to slight differences in the composition of the Co catalysts used in the experiments.

The reaction products are forms with odd and even C numbers (see Table). Gibson and Clarke[78] confirmed the

TABLE. Characteristics of the liquid product of the hydropolymerisation of ethylene.

Fraction	Concentration, wt. %	Concentration of unsaturated compounds, %	Concentration, wt. %	Concentration of unsaturated compounds, %
	according to Ref. 78		according to Ref. 79	
C_5	20	73	11	100
C_6	28	62	18	68
C_7	8	54	17	65
C_8	13	53	13	60
C_9	10	52	9	51
$>C_9$	21	—	32	—

data of Eidus and coworkers[5], who showed that the yield of C_4 and higher hydrocarbons increases with increase in the CO concentration in the range 0.3–5%. The yield of methane does not increase, and the quantity of ethylene converted into ethane decreases from 90% to 35% with increase in the CO concentration from 0.3% to 6.1%.

The distribution of the radioactivity over the individual atoms in the hexene and heptene molecules was determined[78] by a specially developed method for the stepwise degradation of these molecules. The following radioactivity ratios were obtained:

$$\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$
$$2.3 : 6.2 : 40.7 : 41.8 : 7.9 : 1.1$$

$$\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$
$$0.6 : 13.1 : 22.4 : 30.9 : 31.8 : 0.9 : 0.3.$$

The accuracy of these figures increases with increase in the actual figures, from ±30–50% for the values 0.6–2.3 to ±1–5% for the values 30–42. Thus in hexene and heptene the central two or three C atoms respectively have a high radioactivity and the terminal atoms have a low radioactivity. The double bonds lie chiefly between atoms 2 and 3 in hexene and between atoms 2 and 3 or 3 and 4 in heptene.

Gibson and Clarke[78] consider that the mechanisms of chain growth in hydropolymerisation and the formation of hydrocarbons from CO and H_2 are similar. Stepwise attachment of species containing one C atom to the growing chain takes place. The distribution of the radioactivity in the final product is the same as that in the chain with the same C number on the surface. The radioactivities of each C atom 3 and 4 in hexene and heptene correspond to the increase in radioactivity for the attachment of one atom from ^{14}CO. The properties of the radicals produced from CO and from C_2H_4 are different, in agreement with the conclusions reached by Blyholder and Emmett[63].

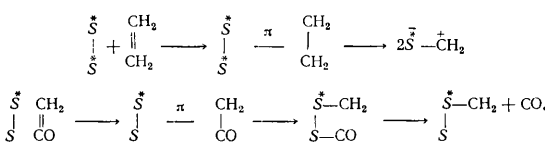
In a study of the radioactivity distribution in propanol, hexene, and heptene, with the assumption that the reactive group (hydroxyl or multiple bond) is the growing end of the chain, Gibson and Clarke[78] reached the following conclusions: (1) chain growth is initiated by the reaction of CO, or an oxygen-containing radical formed from it, with an adsorbed radical produced from ethylene, to give a chain of three C atoms; (2) chain growth involves the attachment, to this radical of three C atoms (or its derivative), of radicals each containing one C atom, and also of oxygen and radicals produced from CO or ethylene. Chain growth does not take place in the absence of oxygen-containing radicals. These radicals, which are produced from ethylene, may be formed from hydrocarbon radicals, if their concentration on the

surface is high, by reaction with adsorbed oxygen, produced according to the scheme proposed by Blyholder and Emmett[63] (see p. 344). The formation, from hydrocarbon radicals, of oxygen-containing radicals active in chain growth apparently explains two observations: firstly, the presence of non-labelled C atoms in the centre of the chains, and secondly the formation of higher hydrocarbons from a mixture of ethylene and hydrogen on a catalyst which has taken part in the reaction of a ternary mixture of C_2H_4, H_2, and CO;[65,66] and (3) chain termination takes place by the reaction of the growing chain with radicals produced from ethylene and containing one or two C atoms.

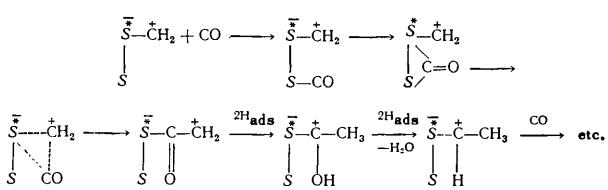
A considerable difference is observed in the influence of the concentration of CO in the original gas in the Fischer–Tropsch reaction and in hydropolymerisation. The latter takes place more slowly with increase in the CO concentration above 5%, apparently due to the adsorptive displacement of the alkene from the catalyst surface, as a result of which the rate of the process is determined by the conversion of carbon monoxide into methylene radicals. The adsorptive displacement of the alkene by carbon monoxide also explains the lower rate of hydropolymerisation of propene[49] and butenes[80,81] at CO concentrations of 10–15%.

On the basis of new radiochemical data, Ronginskii[82] developed his scheme[19] of chain growth (see p. 343) to include methylene radicals or ion-radicals in the primary stage. It is assumed that there exist on the surface unique active centres S, on which the growing chains are fixed. The centres differ in their structure and in the concentration of modifying additives from the other active centres S on which other processes take place, for example, the adsorption of CO and H_2.

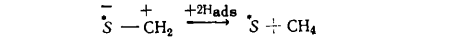
The primary active forms with the properties of chain growth initiators are assumed to be heterogeneous radicals or the simplest carbonium ions $S-CH_2$ or $S-CH_2$, which are formed in particular by the dissociation of ethylene or keten:



The growth of the carbon chains takes place with the participation of CO and H_2 by a number of successive processes of the same type: CO and the methylene ion radical combine on the surface to form a keten molecule which is adsorbed by two C atoms and which is converted into a different adsorbed state — a keten molecule adsorbed only by the C atom of the carbonyl group. Under the influence of hydrogen, the carbonyl group is converted successively into a hydroxymethine group and then into a methine group with the liberation of a molecule of water. Chain growth continues with the attachment of CO, adsorbed on the surface, to the ethylidene ion-radical (see p. 343).



Chain termination takes place by hydrogenation to saturated hydrocarbons:



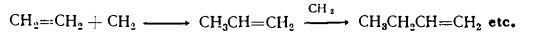
On the basis of the fact that the isotopic effect α_i (H_2, D_2) for the Fischer–Tropsch reaction is 0.77,[83] it was concluded that any stage in which the transition state is formed with the participation of free hydrogen molecules cannot be the rate-determining stage; the same is true of the diffusion, adsorption, and desorption of hydrogen. According to Roginskii[82], the kinetics of the reaction[43] and the fact that the isotopic effect α_i is < 1 show that the limiting stage must be one of the stages in the formation of additional methylene radicals, involving the participation of carbon monoxide and hydrogen in the adsorbed state.

IV. DEGRADATION OF CARBON CHAINS

All the above schemes consider only growing chains. Degradation processes, apart from the dissociation of ethylene into two methylene radicals, which unlike the dissociation of keten into CH_2 and CO has not been experimentally proved, is not considered in these schemes. Experiment shows, however, that degradation processes play an extremely important part in hydropolymerisation[84–86]. It is assumed that the species undergoing decomposition are semi-hydrogenated forms of alkenes consisting of heterogeneous hydrocarbon radicals, and that this decomposition takes place intensively in the presence of CO; this can probably be attributed to the action of radicals containing one carbon atom[87,88]. The formation of radicals with a smaller C number from chains with a large C number is observed particularly clearly in the hydropolymerisation of isobutene[89–98] and higher alkenes such as hex-1-ene[99,100] and oct-1-ene[101]. These processes take place with the participation of hydrogen, the concentration of the latter in the original gas influencing the reaction rate and the composition of the final products[102,103].

It has been noted that the products of the hydropolymerisation of alkenes, in addition to polymeric forms, contain compounds with C numbers which are not multiples of that of the original alkene. Their concentration in the high-boiling fraction of the condensate, which contains hydrocarbons with a C number greater than that of the original alkene, increases with increase in the C number of the latter and has the values (wt.%): 34, 44, 73, 80, and 85 for ethylene, propene, but-1-ene, pent-1-ene, and oct-1-ene respectively[74,104]. This is attributed to the fact that the greater the C number of the original alkenes, the greater the number of "non-multiple" hydrocarbons which can exist; this number is equal to n - 1 when the C number of alkene is equal to n.

Examination of the methods by which higher hydrocarbons with a non-multiple C number can be formed leads to the conclusions that they cannot be formed in such large quantities entirely by hydrocondensation of the original alkene with CO according to the scheme:



Non-multiple hydrocarbons are formed chiefly by rupture of the C–C bonds in the course of the process with the subsequent reaction of the resulting radicals with adsorbed alkene molecules.

The number of molecules of the original normal α-alkene taking part in the formation of higher hydrocarbons and corresponding to one CO molecule taking part in the same reaction (yield with respect to initiator) is usually greater than unity, indicating [105,106] a chain mechanism for the reaction, in good agreement with the radiochemical data examined above. The yield with respect to the initiator decreases with increase in the C number of the original alkene, other conditions being equal. At ratios in the original gas $H_2 : CO \simeq 8$ and $C_nH_{2n} : H_2 \simeq 1$, the yield with respect to initiator is equal to 6–8 for ethylene, ~ 4 for propene, ~ 3 for but-1-ene, and ~ 2 for hex-1-ene [104]. Thus 12 C atoms react for every CO molecule, irrespective of the molecules in which they are present. All these reacting atoms are apparently adsorbed on the catalyst surface; this may lead to some deformation of the carbon chains and bring about an increase in the ease of rupture of the C–C bonds in the reaction with the formation of heterogeneous radicals. Adsorption by all C atoms of the alkene takes place at low concentrations of CO under the conditions of the radical-chain reaction of growth and degradation of the carbon chains. At higher CO concentrations, the C atoms of the alkene which do not adjoin the multiple bond are displaced from the surface by the carbon monoxide being adsorbed. The alkene is then adsorbed only by the C atoms of the double bond without deformation of the other bonds, and chain growth takes place by a hydrocondensation scheme without rupture of the C–C bond (see p. 346). Thus depending on the concentration of CO and H_2 in the original gas and the adsorption properties of the alkene, one form of adsorption is replaced by the other, as a result of which the hydropolymerisation is replaced by hydrocondensation [107].

V. INITIATED HETEROGENEOUS-CATALYTIC REACTIONS

The heterogeneous-catalytic reaction examined above, namely the hydropolymerisation of alkenes in the presence of hydrogen, is initiated at 190–200° by small quantities of CO. A new heterogeneous-catalytic reaction, taking place only in the presence of initiator, was discovered recently. This is the hydropolymerisation of alkenes, initiated at 100–120° by small quantities of oxygen in the presence of hydrogen on Co catalysts [108-113]. Under the optimal conditions, this reaction takes place to the extent of 35–45%, and the hydrogenation of the alkene to the alkane with the same number of carbon atoms takes place to the extent of 17–30%, calculated on the original alkene (C_2–C_4). The optimal concentration of oxygen in the original alkene–hydrogen mixture amounts to ~ 2%. Hydropolymerisation under the influence of oxygen always takes place at the same time as hydrogenation of the alkene. A catalyst which is inactive with respect to hydrogenation is also inactive with respect to hydropolymerisation. As with the hydropolymerisation of alkenes initiated by carbon monoxide, the initiation of the hydropolymerisation by oxygen is followed by the formation of new intermediate active forms on the catalyst surface, indicating degradation processes. In addition to true polymeric forms, the reaction products contain hydrocarbons in whose molecules the numbers of carbon atoms are not multiples of the number in the original alkene. The results obtained have made it possible to develop the concept of "initiated heterogeneous-catalytic reactions" [114], an example of which is provided by the hydropolymerisation of alkenes under the influence of CO or O_2. A characteristic feature of initiated heterogeneous-catalytic reactions is that they take place entirely on the surface of the solid catalyst and that they require not only a specific catalyst but also the presence, in the reaction zone, of a compound which differs from the direct starting materials and which does not react in stoichiometric proportions. This compound starts the reaction and acts as initiator. The initiator may or may not take part in the development of the process and the formation of the final products, depending on the reaction conditions.

Conditions were found under which CO undergoes almost no reduction by hydrogen and is not included in the final products of the hydropolymerisation of ethylene at 190°. The quantities of CO taken for the reaction and obtained after the reaction were identical. The yields and compositions of the reaction products, however, differed little from those observed in the reaction involving the reduction of CO. The reaction does not take place in the absence of CO.

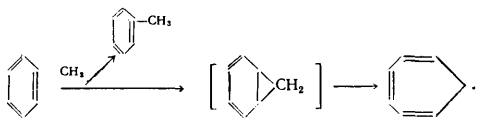
The $C_2H_4 : H_2$ ratio in the original gaseous mixture has a characteristic influence on the reduction of CO in the hydropolymerisation of ethylene. When this ratio is less than 1.0–1.2, CO reacts to the extent of 60%, but when the ratio is greater than 1.7, the CO is not used up. In the hydropolymerisation of propene, butene, and isobutene, the CO is reduced and used up in the reaction. In the joint hydropolymerisation of ethylene and its homologues, the quantity of CO used up is greater, the smaller the volume ratio of ethylene to hydrogen in the original gas [115].

It is possible to picture several ways in which hydropolymerisation is initiated by carbon monoxide. One possibility is that the carbon monoxide is reduced to some extent to surface intermediate products of the methylene and oxymethylene radical type, which take part in the initiation, and also possibly in growth of the carbon chains, so that they appear in the final products. During the reaction, the CO is regenerated, and the molecules of the regenerated CO may contain carbon atoms which come not from the original CO but from the alkene. Another way in which the reaction may be initiated by carbon monoxide does not involve the participation of CO at the start of formation and growth of the hydrocarbon chains and hence does not involve introduction of its carbon atoms into the final products. This takes place when the adsorption is hindered by a high concentration of ethylene. It may be assumed that in order to take part in the reaction in the form of CH_2, CHOH, and similar radicals or in the form of CO, the carbon monoxide should be adsorbed by both the C and O atoms. When adsorption is hindered, this is unlikely, and the CO is adsorbed through only the C atom. In this adsorbed form reduction is probably impossible, but the formation of $CO.nH_2$ complexes on the catalyst surface is still possible, and in these complexes the active hydrogen is capable of reacting with an alkene molecule, converting it into a heterogeneous radical which initiates the hydropolymerisation.

The hydropolymerisation of ethylene without consumption of CO and hence without the liberation of water indicates that the formation of hydrocarbon chains is in principle possible not by a dehydration-condensation scheme [29] but by a polymerisation scheme with a correction for degradation processes [86,87]; this is extremely important for an understanding of the mechanism of the reaction.

VI. HYDROCONDENSATION OF CARBON MONOXIDE WITH CYCLIC HYDROCARBONS

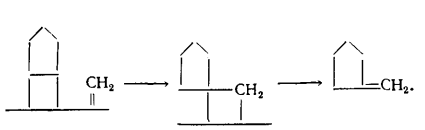
The catalytic hydrocondensation of carbon monoxide with alkenes [40] is one of the first stages of the Fischer–Tropsch reaction and the hydropolymerisation of alkenes under the influence of CO. It is also of independent importance, however. It demonstrates the ability of CO, mixed with H_2, to act as an alkylating agent, particularly a methylating agent, leading to the formation of the homologues of alkenes. Hydrocondensation takes place selectively with cyclic hydrocarbons, although the yields are low, since these hydrocarbons do not undergo further hydropolymerisation. This reaction was first used to prove the formation of surface methylene radicals from CO and H_2 on a skeletal Co–Ni catalyst during the conversion of benzene into toluene [116]. The formation of toluene from benzene, CO, and H_2 was also observed [117] over an Fe–Cu catalyst. When the same reaction was carried out at 190° and 1–20 atm (Co–ThO_2–kieselguhr catalyst) the reaction products were found to contain small quantities of cycloheptatriene in addition to toluene [118]. Its formation was attributed to the reaction of methylene radicals with benzene with the intermediate production of the norcaradiene structure:



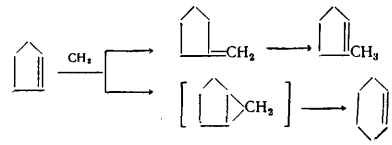
The formation of cycloheptatriene and toluene from benzene, CO, and H_2 takes place by parallel reactions [119].

A mixture of cyclohexene, CO, and H_2 gave up to 10% of the monomethyl and dimethyl derivatives [120,121]. Cyclopentadiene, CO, and H_2 gave 4–5% of the monomethyl, dimethyl, and trimethyl derivatives [122].

The hydrocondensation of CO with cyclopentene gave a mixture of hydrocarbons with C number greater than that of the original cycloalkene, in yields of 33% relative to the CO reacting or 5% with respect to the cyclopentene passed. After complete hydrogenation, the product was found to contain 45% methylcyclopentane, 20% ethylcyclopentane, 8% propylcyclopentane, and 27% cyclohexane hydrocarbons (10% cyclohexane, 10% methylcyclohexane, and 7% ethylcyclohexane) [74,123]. The process involving increase in the size of the ring is associated directly with the hydrocondensation [75]. It was shown [126] that the formation of a six-membered ring from a five-membered ring is not associated with isomerisation of the five-membered ring or with the formation of methylenecyclopentane according to Herington's scheme [34]:



It was suggested [124] that by analogy with the formation of cycloheptatriene from benzene via the norcaradiene structure, hydrocarbons with a six-membered ring are produced from cyclopentene with the intermediate formation of the bicyclo[1,0,3]hexane structure:



The ease of alkylation decreases in the order: cyclopentene > cyclohexene > benzene. Alkylation is favoured by a decrease in the concentration of CO in the original gas from 20% to 5%. [125]

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From the present review it may be concluded that in the preparation of hydrocarbons from CO and H_2, the latter form a primary complex (the C_1 complex) on the catalyst surface, and that the growth of the carbon chain begins from this complex. Chain growth involves the successive attachment of structural units containing one carbon atom to the primary complex. Experiments with the addition of a small quantity of compounds labelled with ^{14}C to the CO–H_2 mixture show that these compounds can be divided into two groups. The reaction with compounds of the first group gives liquid products whose molar radioactivity increases regularly with increase in the C number of the fraction. These compounds include formaldehyde, methanol, methyl formate, and keten labelled in the CO group. The reaction with gas containing compounds of the second group gives liquid products whose molar radioactivity remains constant with change in the C number. These compounds include ethanol, propanol, acetaldehyde, propanal, ethylene, propene, and keten labelled in the CH_2 group. These apparently take part in the formation of a primary complex which is analogous to or identical with the C_1 complex, either as the complete molecule or as a part of the molecule containing the labelled ^{14}C atom. For example, keten enters the primary complex in the form of the CH_2 group, and ethylene enters completely (or, less probably, as a CH_2 radical formed by the dissociation of $CH_2{=}CH_2$); alcohols enter the complex completely on Fe catalysts but in the form of the dehydration product (the alkene) on Co catalysts. Substances of the first group undergo preliminary decomposition with the formation of CO, which reacts further, taking part in chain growth. When added in larger quantities, ethylene may be included in the chain during its growth. This shows that a structural unit with two or more C atoms may also take part in chain growth. In the same way, the primary complex may contain not merely one, but also two or more C atoms. The initiation of the chains by methylene radicals formed by dissociation of keten shows convincingly that the presence of an oxygen-containing radical is not essential for chain initiation. This process also takes place with the participation of a hydrocarbon radical. The primary complex apparently may or may not contain oxygen, depending on the conditions; there is then an increase in the probability of the condensation or polymerisation scheme for C–C bond formation.

The fact that chain growth under certain conditions takes place exclusively according to the polymerisation scheme and not by condensation with the liberation of water is shown by new data, according to which the hydropolymerisation of ethylene under the influence of CO takes place under certain conditions with almost no consumption of the latter, and hence without the liberation of water.

It has been shown that degradation processes play an important part in the formation of carbon chains. The hydrocondensation of unsaturated hydrocarbons with CO may take place not only with the formation of a straight chain, but also via three-membered complexes analogous to the products of the reaction of multiple bonds with carbenes.

The concept of initiated heterogeneous-catalytic reactions has developed; according to this concept, an important part is played not only by the solid catalyst but also by an initiator which is not involved in the stoichiometry of the reaction.

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PHASE EQUILIBRIA BETWEEN IMMISCIBLE GASEOUS PHASES

D.S.Tsiklis and L.A.Rott

INTRODUCTION

Until very recently there were reckoned to be five types of equilibria: crystal–crystal, crystal–liquid, crystal–gas, liquid–liquid, and liquid–gas. The theory of these phase equilibria was developed by Konovalov[1], Stoletov[2], Gibbs[3], van der Waals[4], Kuenen[5], and others. There was also convincing experimental confirmation of the theoretical predictions.

It now seems astonishing to us why the possibility of the existence of yet another type of equilibrium — gas–gas equilibrium (the existence of which could have been postulated even by simple analogy) — was generally not discussed right up to the end of the XIXth century. Even at the time of Dalton, scientists were surprised[6] that gases did not behave as liquids and did not take up positions in relation to one another according to their specific gravities. The explanation for such behaviour of gases was found in the fact that at low pressures they are mechanically (energetically, in modern terminology) independent.

The concept of the energetic independence of gases, true only at moderate pressures, greatly suppressed interest in a search for equilibrium between gaseous phases. Even after van der Waals[7] and Kammerlingh-Onnes and Keesom[8] had made, in the 1890's, a theoretically based prediction of the possibility of the existence of such an equilibrium, about 50 years elapsed before the first experimental work appeared, carried out by Krichevskii[9]. The results completely confirmed the predictions of the Dutch scientists.

Such a prolonged break is explained not solely to the viability of the concept of the energetic independence of gases. van der Waals and his students correctly predicted that the phenomenon of restricted mutual solubility of gases is possible because there is a great similarity between liquids and strongly compressed gases. Hence it seemed natural to search for this phenomenon at high pressures. The absence of the technical means necessary for this was a second reason, which for long delayed the experimental confirmation of this interesting phenomenon. However, as we shall see subsequently, it can also be observed at comparatively low pressures.

But somehow or other, if the honour of the theoretical prediction of and basis for the new type of equilibrium belongs to the Dutch scientists, that of resurrecting their forgotten ideas, experimentally verifying these ideas, and developing further the theory of phase equilibria with allowance for this new equilibrium belongs wholly to Soviet scientists[10].

RESTRICTED MUTUAL SOLUBILITY OF GASES

The works of van der Waals and his coworkers contained not only an indication of the possibility of equilibrium between two gaseous phases at temperatures above the critical temperatures of the two components of a binary mixture but also predictions about the form of the critical curve.

According to these predictions two types of such equilibria are possible. *The first type* (to which belong systems containing helium) is characterised by the critical curve (in coordinates of pressure and temperature) in leaving the critical point of the less volatile component (Fig. 1) being directed towards the side of high temperatures. The curve is convex towards the temperature axis and at the point *M* turns towards lower temperatures. The reversal occurs at appreciable pressures and after it the curve is directed towards the side of the critical point of the more volatile component. Fig. 2 shows the phase diagram for this type of equilibrium.

Second type. On leaving the critical point of the less volatile component, the critical curve (Fig. 3) is at first directed towards the side of lower temperatures. The curve is convex towards the temperature axis and passes through a minimum — point *D*. Its name, according to van der Waals terminology, is the double homogeneous point. Then the curve turns towards the side of high temperatures and subsequently its form does not differ from that described for the first type†.

Fig. 4 shows a phase diagram for this type of equilibrium as we visualise it now. In the temperature region from the critical temperature of the less volatile component to the temperature of the double homogeneous point both liquid–gas and gas–gas equilibria exist. In the temperature region from the critical point of the less volatile component up to the temperature maximum *M* there is only gas–gas equilibrium.

METHOD OF INVESTIGATION

Phase equilibria between two gaseous phases have been investigated by analytical and synthetic methods. These methods (details of the apparatus and experimental technique) have been described in sufficient detail already[12]. Here it is possible only to mention that by analytical is meant those methods in which the compositions of the coexisting phases are determined by the analysis of specimens taken from each phase. In working by synthetic methods a mixture of the two components of known quantitative composition is made up and then the moment for the disappearance or appearance of one of the phases is observed, by measuring the temperature, pressure, or volume (or all three parameters) of the system.

Many of the studies carried out in our country employed analytical methods in equipment with a mercury piezometer (Fig. 5) (a Callietet tube[13]). The piezometer is a metal

† We will not deal with the form of the critical curve in the region close to the critical point of the more volatile component (see, for example, Vogel[11]).

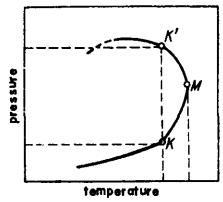


Fig. 1. Critical curve of systems giving the first type of separation. K critical point of the less volatile component; M maximal temperature of existence of gas–gas equilibrium; K' upper critical point of the gas–gas equilibrium.

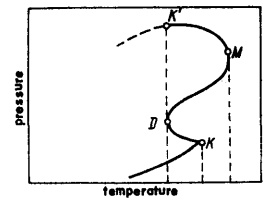


Fig. 3. Critical curve of systems giving the second type of separation. K critical point of the less volatile component; D double homogeneous point; M maximal temperature of existence of gas–gas equilibria; K' upper critical point for the gas–gas equilibrium.

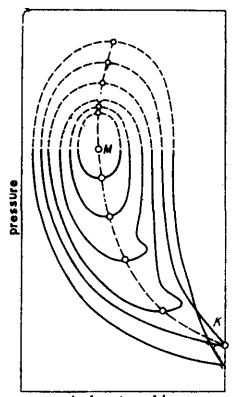


Fig. 2. Phase diagram of the gas–gas equilibrium of the first type.

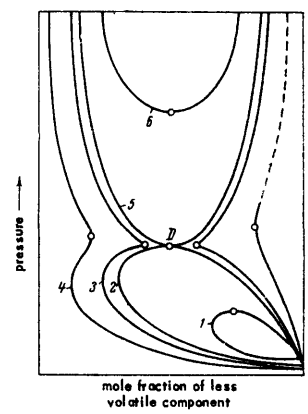


Fig. 4. Phase diagram of the gas–gas equilibrium of the second type. 1)–4) liquid–gas equilibrium curves; 5), 6) gas–gas equilibrium curves.

separating funnel filled with mercury. A mixture of known composition which is being studied is prepared outside the apparatus, run into the piezometer [14], and the temperature and pressure for the experiment created in the apparatus. Layering takes place. The upper phase is forced out by the mercury through the upper valve and is analysed. After all the upper phase has left the lower phase is forced out. The operations of forcing out the phases are carried out at constant pressure produced by pumping mercury from beneath into the piezometer under the pressure of a working fluid, which is supplied by a multiplier (Fig. 6).

The use of mercury at temperatures above 200°C is undesirable, both from the standpoint of accident prevention and also because it is soluble in compressed gases. Therefore, mercury-free equipment is used [15–18]. In this, the mixture is created in a high pressure vessel fitted with an electromagnetic stirrer and the compositions of the phases are determined by withdrawing specimens of the phases from above and below the vessel (Fig. 7).

Arons and Dipen [19] used the synthetic method for investigating gas–gas equilibria in the helium–xenon system. They prepared a mixture of xenon and helium of known concentration and filled a glass piezometer with it. The piezometer was put in a high pressure vessel with a sight glass (Fig. 8). The mixture in the piezometer was compressed by mercury. The phase diagram of the system could be constructed from observations of the appearance and disappearance of a meniscus and by noting the pressures corresponding to the appearance and disappearance of a bubble of the upper or lower phase. The volumes of the coexisting phases could also be measured with this apparatus.

Gas–gas equilibrium of the first type starts at the critical point of the less volatile component, which is usually found at moderate temperature and pressure. Making use of this, Krichevskii proposed, and Khodeeva [20] put into practice, a method in which the less volatile component is introduced into a glass ampoule of known capacity in such a quantity that it is at its critical volume. The critical temperature of the substance is measured and then a small quantity of the second component is added and the critical temperature of the mixture again measured. If the critical temperature is higher — that is, the meniscus between the phases disappears at a higher temperature — than the critical temperature of the pure component (less volatile), then a region of gas–gas equilibrium of the first type must exist in the system.

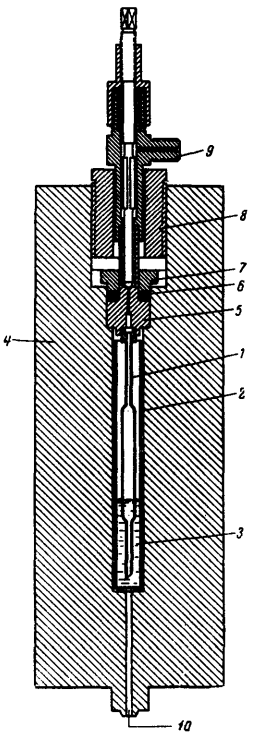


Fig. 5. Drawing of the high-pressure vessel with piezometer:
1) metal piezometer (Callietet tube); 2) beaker; 3) mercury; 4) high-pressure vessel; 5) head seal; 6) packing; 7) gland nut; 8) female screw; 9) valve for withdrawing specimens; 10) working liquid for multiplier.

REVIEW OF THE EXPERIMENTAL DATA

After Krichevskii and his coworkers[21-23] had observed the phenomenon of restricted mutual solubility of gases, another 25 systems with a region of phase equilibria between two gaseous phases were found. Table 1 lists all the systems‡.

Table 1 shows that all the systems with helium give layering of the first type. Layering of the second type is usually observed in systems containing a polar component. An exception is water: layering of the first and of the second type is observed in systems with water.

We will discuss two systems in greater detail: helium–carbon dioxide, as a representative of systems giving the first type of layering, and ammonia–nitrogen, a system with the second type of layering.

The $He-CO_2$ system[24] was studied at temperatures from 25° to 100°C and pressures up to 10 000 at. Figs. 9 and 10 give the phase diagram and critical curve and repeat the picture represented in Figs. 1 and 2, with the difference that the critical curve of the real system does not return towards lower temperatures as the pressure is raised.

‡ It is evident from the table that the great majority of investigations of this phenomenon have been made in the Soviet Union.

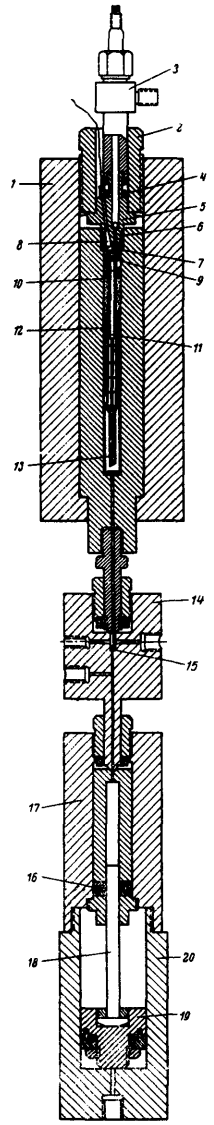


Fig. 6. Drawing of apparatus for investigating the equilibrium between two gas phases at pressures of up to 20 000 at:
1) double-walled high-pressure vessel; 2) female screw; 3) valve; 4) isolating ring; 5) head seal; 6) packing; 7) exhaust ring; 8) electrical entry; 9) head piezometer; 10) solenoid; 11) stirrer armature; 12) beaker with mercury; 13) spring; 14) valve box; 15) reversing valve; 16) packing for piston of multiplier; 17) cylinder of high-pressure multiplier; 18) high-pressure piston; 19) low-pressure piston; 20) low-pressure cylinder.

At temperatures less than the critical temperature of CO_2 liquid–gas equilibrium is observed. The curves of this equilibrium (the curve for the solubility of helium in liquid carbon dioxide and that of the latter in compressed helium) start at a point corresponding to the saturation vapour pressure of CO_2 at the given temperature. At temperatures

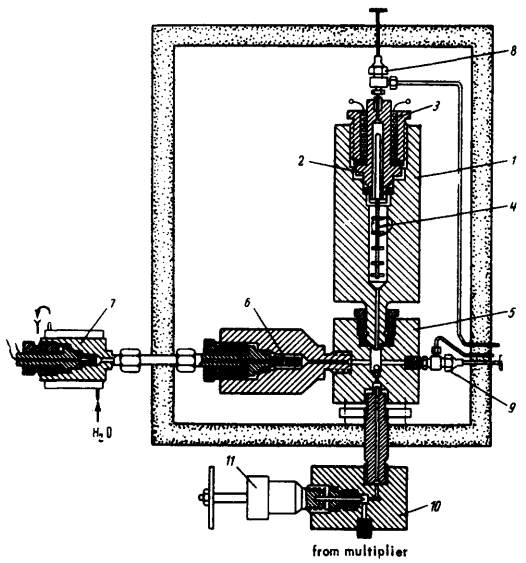


Fig. 7. Drawing of mercury-free apparatus for investigating gas–gas equilibria at high pressures and temperatures:
1) high-pressure vessel (EI437B steel); 2) seal; 3) solenoid; 4) stirrer; 5) valve box; 6) bellows for protection of the manganin manometer; 7) manganin manometer; 8) valve for removing upper phase; 9) valve for removing lower phase; 10) valve box; 11) press valve.

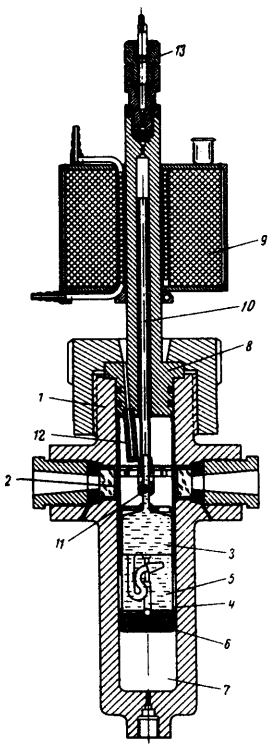


Fig. 8. Drawing of apparatus for investigating gas–gas equilibrium by a synthetic method:
1) high-pressure vessel; 2) sight window; 3) piezometer with gas mixture; 4) inner part of telescope tube; 5) mercury; 6) piston; 7) water; 8) seal; 9) solenoid; 10) armature of electromagnetic stirrer; 11) permanent magnet; 12) thermocouple pocket; 13) valve.

TABLE 1. Systems in which gas–gas equilibrium has been observed.

System	Intervals of investigation		Reference	Type of gas–gas equilibrium
	temperature, °C	pressure, at		
Ammonia–nitrogen	90—175	16 000	21—23,25	second
Ammonia–methane	45—100	10 000	23	second
Ammonia–nitrogen–hydrogen, three compositions with 22, 50, and 75 % hydrogen in the mixture without ammonia	90—120	5 500	23	second
Ammonia–nitrogen–methane with 20 and 80 % methane	55—110	5 500	26	second
Ammonia–argon	70—140	10 000	27	second
Nitrogen–sulphur dioxide	35—40	9 000	28	second
Helium–ammonia	125—175	10 000	24	first
Helium–carbon dioxide	25—100	10 000	24	first
Helium–ethylene	25—150	10 000	29	first
Helium–propane	100—150	7 000	30	first
Helium–benzene	300	1 000	31	first
Helium–methanol	245	3 000	31	first
Helium–hexane	245	3 000	31	first
Helium–sulphur dioxide	175—200	7 000	31	first
Helium–xenon	5—65	2 000	19	first
Helium–acetylene	36	64	20	first
Helium–ethane	32	51	20	first
Water–butane	200—430	6 000	15	first
Water–nitrogen	300—350	6 000	32	second
Water–carbon dioxide	250—350	3 500	16,17	second
Water–argon	350—400	4 000	33	second
Helium–dinitrogen monoxide	37	74	34	first
Helium–Freon-12	25—122	330	35	first
Helium–Freon-22	100	330	36	first
Helium–Freon-114B2	216—223	330	36	first
Helium–butane	—	—	37	—
Water–benzene	265—300	700	38	second
Water–n-heptane	295—355	700	38	second
Water–n-pentane	300—352	700	38	second
Water–2-methylpentane	300—355	700	38	second
Water–toluene	280—310	700	38	second

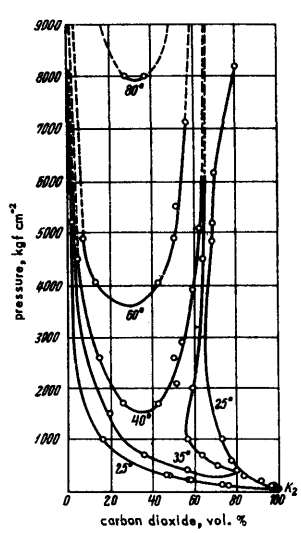


Fig. 9. Gas–gas and liquid–gas equilibria in the helium–carbon dioxide system.

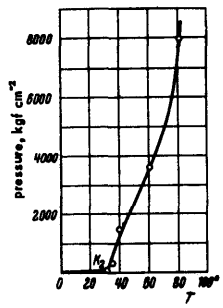


Fig. 10. Critical curve in the helium–carbon dioxide system.

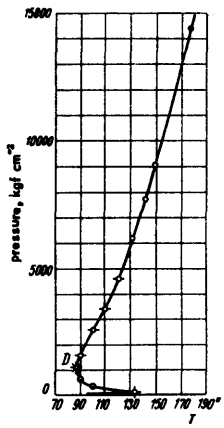


Fig. 12. Critical curve in the ammonia–nitrogen system. The symbols are the same as in Fig. 11.

greater than the critical temperature of CO_2 the curves leave the ordinate axis and form a characteristic horn. As the temperature is raised the horn is gradually obliterated.

The NH_3-N_2 system. This system was studied at temperatures from 90° to 175°C and pressures up to 16 000 at. Figs. 11 and 12 give the phase diagram and critical curve, which are similar to Figs. 3 and 4, except for the form of the curve at higher temperatures and pressures.

We will consider in greater detail the phase diagram of such a system represented three-dimensionally (Fig. 13) in the coordinates pressure–composition–temperature. Two regions of phase equilibria are clearly evident here: liquid–gas equilibrium and gas–gas equilibrium. The loops of the liquid–gas equilibrium start on the vapour pressure curve of the less volatile component (here, ammonia). The composition region occupied by these branches decreases with rise in temperature and shrinks to a point at the critical

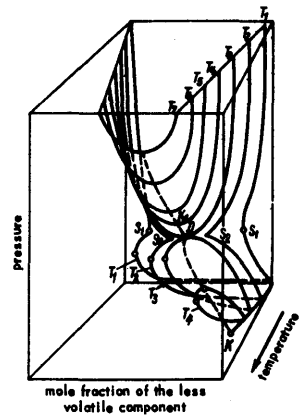


Fig. 13. Space diagram for systems which give the second type of layering.

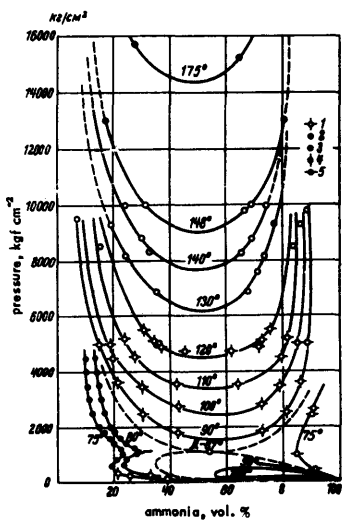


Fig. 11. Liquid–gas and gas–gas equilibria in the ammonia–nitrogen system. Data from: 1) Ref. 21; 2) Ref. 23; 3) Ref. 25; 4) Ref. 39; 5) Ref. 40.

point of the less volatile component. The gas–gas equilibrium curves are situated in the same composition interval but at other pressures. The region of this equilibrium also extends to the side of temperatures higher than the critical temperature of the less volatile component.

The point corresponding to the temperature minimum on the critical curve is clearly evident on the diagram. This is point D, at which the gas–gas and liquid–gas equilibrium curves touch. In van der Waals terminology it is called the binary homogeneous point§. The binary homogeneous point is a singular point. On raising the temperature above the temperature of this point the equilibrium loop breaks into two parts — the curves of the gas–gas and liquid–gas equilibria. On reducing the temperature below the temperature of the binary homogeneous point breaking of the loops also takes place, but now it is along the pressure axis. As a result fantastic forms of the solubility curves

§ This terminology is derived from the theory of folds[41] on the basis of which the existence of the types of gas–gas equilibria was also predicted.

for gas in liquid (right branches) and liquid in gas (left branches) are produced. It can be noted from this that at the moment of the break (longitudinal) points of return (S_2) appear on the curves; these points then degenerate into the points of the solubility maxima for gas in liquid and liquid in gas (S_1).

Fig. 13 shows that the solubility curves for gas in liquid and liquid in gas have a very complex form, especially close to the binary homogeneous point. The solubility of gas in liquid under pressure first increases with the pressure, passes through a maximum, decreases, and then (if the possibility of the existence of an upper critical point of gas–gas equilibrium is considered) should start to rise again.

The solubility of liquid in gas at first decreases with rise in pressure, passes through a minimum, starts to rise, reaches a maximum, falls again, subsequently hardly changes with the pressure, and finally (if the upper critical point is considered) can start to rise again.

This complex form for the curves has a theoretical explanation[10]. The fact is that both the minimum and the maxima on the solubility curves for liquid in gas and gas in liquid are points at which the partial molar volume of the substance and its molar volume become equal¶.

At low pressure the partial molar volume of a substance in its infinitely dilute solution ($\overline{v}_2'$) is much greater than the molar volume of the substance in the condensed phase v_2^0. But with increase in pressure the value $\overline{v}_2'$ rapidly approaches v_2^0 and becomes equal to it since the compressibility for $\overline{v}_2'$ is greater than the compressibility for v_2^0. In this a liquid in gas solubility minimum is observed. At still higher pressures $\overline{v}_2'$ becomes less than v_2^0 and the solubility starts to rise. However, this decrease cannot be continued indefinitely. With rise in pressure the intermolecular interaction starts to increase. Therefore the partial molar volume of the substance in the gas phase begins to increase. It again becomes equal to the molar volume and a solubility maximum appears on the curve.

Similar arguments show that the gas-in-liquid solubility maximum occurs at a pressure when the molar volume of the gas being dissolved equals the partial molar volume of this gas dissolved in the liquid.

Fig. 13 shows clearly that the presence of gas–gas equilibrium curves allows all the known facts about phase equilibria in binary systems to be explained. For example, it becomes quite clear that the gas–gas equilibrium curves do not start and do not end on the vapour pressure curves of the less volatile component and have nothing in common with the liquid–gas equilibrium curves. It is also understandable that the points of the maxima and minima on the curves are degenerate points of reversal formed from the double homogeneous point. Hence it can be concluded that if a solubility maximum is found in investigating the solubility of a gas in a liquid, a region of gas–gas equilibrium should occur in that system.

We will return briefly to the question of the reversal of the critical curve. On considering solutions of helium as intrusion solutions, Tsiklis and Zhukhovitskii[42] showed that here there is generally no reason to expect reversal. This, however, does not signify that it cannot happen in other instances. But if such a reversal is possible in principle, then it should occur at rather high pressures, when the solubility of the gas again starts to increase with pressure owing to a further change in the partial molar and molar volumes. But at such high pressures crystallisation of the gases can begin. In this instance the critical curve generally will not be continuous. The gas–gas equilibrium changes into a new form of equilibrium — crystal–gas equilibrium (Fig. 14).

On considering the experimental data on gas–gas equilibrium in the systems investigated it is noticeable that for each of the types (first and second) the experimental results repeat Figs. 2 and 4 well. They differ, of course, in the parameters of the curves and especially in the coordinates of the double homogeneous point and the temperature interval between it and the critical point of the less volatile component. In this respect the water–nitrogen system is especially characteristic. In it the binary homogeneous point is at 364°C, that is, 10 deg below the critical temperature of water. For the ammonia–nitrogen system it is at 87°C, that is, 46 deg below the critical temperature of ammonia; and in the CO_2–H_2O system it is at 260°C, that is, 108 deg below the critical temperature of water.

To conclude the discussion of the existing experimental data it is necessary to add the following. Visual observations have been made of the helium–ethylene system[29]; the layering process takes place instantaneously. Initially during the compression of a homogeneous mixture strong eddy currents, similar to convection currents, are observed. On reaching the pressure at which layering occurs a sharp visible meniscus appears (Fig. 15). Its appearance is rapid and is accompanied by a fall of "rain" from the drop of heavier phase. The presence of a meniscus contradicts the conclusion that gas–gas equilibrium is a phase transformation of the second order[43].

The surface tension at the boundary of separation in the helium–ethylene and helium–carbon dioxide systems was measured in an analogous apparatus with sight glasses by the capillary method[44]. It was found that, for example, in the helium–ethylene system at 600 at and 18°C the surface tension is ~ 0.5 erg cm^{-2}.

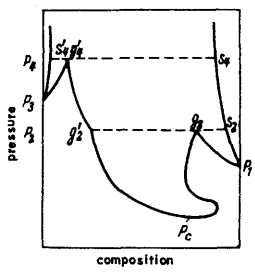


Fig. 14. Gas–gas and crystal–gas equilibria in systems of the first type. P_1 pressure of crystallisation of the pure less-volatile component; P_2 pressure at which the gas phases g_2' and g_2 and the solid phase s_2 are in equilibrium; P_4 pressure at which the two solid phases s_4' and s_4 and one gas phase g_4' are in equilibrium.

¶ Here it is necessary to consider the solvent to be a pure substance.

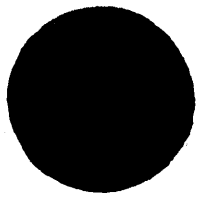


Fig. 15. Meniscus in the helium-ethylene system.

The surface tension in these systems increases with pressure and decreases with rise in temperature. The dependence of σ on P can be represented by the equation:

$$\sigma = \alpha(P - P_c)^2,$$

where α is a constant and P_c the critical pressure. Fig. 16 shows that this condition is obeyed over a wide range of pressures.

Finally, mention must be made of another interesting phenomenon, which is observed in systems with a restricted solubility of gases. We refer to the barotropic phenomenon. This is that with increase in pressure the upper phase becomes heavier and sinks in the lower. Close to the critical point (any equilibrium) the curve in coordinates v (specific volume of the phase on the curve of coexistence) and N_2 (composition) is to the first approximation a parabola with its axis perpendicular to the tangent through the critical point. The gas–gas equilibrium curve (for the second type) in coordinates of pressure against composition is symmetrical with respect to the axis passing through mole fraction 0.5. Therefore an analogous picture will be observed for curves plotted in coordinates of v and N_2.

Fig. 17 shows the liquid–gas and gas–gas equilibrium curves in coordinates v and N_2. A liquid phase of composition A_1 will be in equilibrium with gas phase A_2. At higher pressure the phase of composition B_1 is in equilibrium with a gas phase of composition and volume B_2. On approaching the binary homogeneous point tne difference in volumes decreases and close to the critical point of the gas–gas equilibrium the specific volumes of the coexisting phases become equal (D_1 and D_2). Then the phase in which there is more of the component with higher molecular weight also has the highest specific gravity. Subsequently the volumes of the phases again become unequal but now the volume of the phase containing the component with higher molecular weight diminishes more rapidly and the barotropic phenomenon intensifies.

Hence, the barotropic phenomenon can occur when the molecular weight of the liquid is less than the molecular

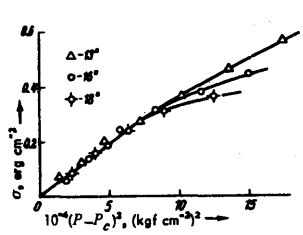


Fig. 16. Variation of σ with $(P - P_c)^2$.

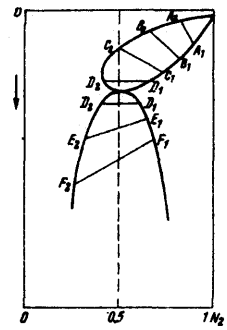


Fig. 17. The barotropic phenomenon.

weight of the gas and the form of the gas–gas equilibrium curve is such that the chords joining the coexisting phases can become parallel to the composition axis.

The barotropic phenomenon was first observed by Kammerlingh-Onnes [45] in investigating liquid–gas equilibrium in the hydrogen–helium system at 20.1°K. In investigations of gas–gas equilibria the barotropic phenomenon has been observed in the ammonia–nitrogen, ammonia–nitrogen–hydrogen (with 22% hydrogen), and ammonia–nitrogen–methane (with 17% methane) systems and also in the argon–ammonia [27,46], water–carbon dioxide [16,17], and water–argon [33] systems.

Despite the fact that the molecular weight of water is less than that of butane, the barotropic phenomenon is not observed in this system†. Evidently it is very important that the form of the phase curve should permit the condition of lines parallel to the composition axis to be fulfilled.

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An isotropic substance at temperatures greater than critical is usually called a gas. Therefore the equilibrium state of the two gaseous phases in the above systems can unreservedly be considered to be gas–gas equilibrium. The credit for the theoretical basis for the equilibrium existence of two gaseous phases at supercritical temperatures is due to Dutch physicists, as mentioned above. However, the possibility of such a state in a system was discussed independently of them, but subsequently. Thus Randall and Sosnik [47] considered gaseous solutions of argon in ethylene at supercritical temperatures. On plotting the activity γ of a component against its mole fraction they concluded that an increase in the constant a in the Hildebrand equation could lead to the mathematical conditions necessary for the separation of the mixture into two phases. However, for this the value of $\log\gamma$ should rise to the same value, which they considered improbable. In the final analysis these authors were convinced of the impossibility of phase separation.

Shottky [49], starting from general ideas about the reasons for the breakdown of a homogeneous mixture into two phases, admitted the possibility of the existence of gas–gas equilibrium at high pressures. Evidently, neither Shottky

† This confirms the correctness of the experimental data according to which a gas–gas equilibrium of the first type is observed in the system (concerning which Schneider [48] has doubts, in relation to Connoly's work [38]).

nor Randall and Sosnik knew of van der Waals' work and expressed their views before the appearance of experimental works in this field.

Even after these works had been published, Dodge[50] wrote, in 1944, ".... systems consisting of gases and vapours are always homogeneous. No one has ever observed more than one gaseous phase". However, Lindros and Dodge[18] subsequently repeated the investigation of the ammonia–nitrogen system, and on finding layering, were convinced of Dodge's error.

Hildebrand[51] wrote, in the third edition of his book: "gases are infinitely miscible and hence raise no problems of miscibility...."‡.

Nobody can now dispute that at temperatures above the critical temperatures of both components a region where the system is heterogeneous can exist. But some authors consider that the phenomena observed should be called equilibrium between two liquid phases[52,53], since the density of the phases at high pressures hardly differs from the liquid density. Others[54,55] assume that this is equilibrium between gas and liquid. Schneider[48] says: "the so-called gas–gas equilibrium" and cannot imagine why the critical curve for liquid–gas equilibrium changes smoothly (for the first type) into the gas–gas equilibrium curve. Discussion on this has been published (see Krichevskii and Tsiklis[56]) but cannot be given in this article.

Here it is proper to state the following. It becomes clear from Fig. 13 that gas–gas equilibrium has no relation to liquid–gas equilibrium. The fact that in a single region of temperature but at different pressures there are two phase equilibrium curves does not signify at all that both phase equilibria are of the same type. It is known, for example, that in the temperature region through which passes a liquid–vapour equilibrium curve there may also pass the liquid–liquid equilibrium curve. But no one ascribes these equilibria to the same type on this basis. Incidentally, Schneider[48] admits that the critical curve for liquid–gas equilibrium can be curved and change continuously into the critical curve of liquid–liquid equilibrium. But if this is possible, then why should change to gas–gas equilibrium be impossible?

van der Waals and Kohnstamm[57] wrote: ".... Hence it follows that (as Kammerlingh-Onnes and Keesom noted) in this instance with strict observance of terminology it is necessary to speak of the equilibrium of two gaseous phases. Actually, there is no basis for calling one of the two phases liquid in a completely closed fold and therefore here one must speak of gas–gas equilibrium at all temperatures exceeding the critical temperature of the second component".

It must be stated once again that liquid–gas equilibrium is the most incorrect name: the equilibrium investigated does not begin and does not end on the liquid–gas equilibrium curve of a pure component. To this it can be added that this question has been discussed repeatedly[58]. Quite recently Rowlinson[59] produced weighty evidence in support of the name gas–gas.

‡ It is interesting in this connection to note that recently Mal'nev and Pekar[68], who considered theoretically a gas in which a high percentage of the molecules are excited to the same electronic energy level (for example, in a laser regime), showed that owing to the anomalously large intermolecular forces the layering of such a gas into two phases of different (in the number of excited molecules) composition is possible. This separation can occur even at atmospheric or even lower pressures.

SOME QUESTIONS OF THEORY

As experimental results accumulate it becomes more and more necessary to give a theoretical explanation for the observed experimental facts.

The problem of the prediction of the possibility of layering of gas mixtures and even pre-calculating the parameters of the critical points of the layering would be solved relatively simply if there was an equation of state giving the behaviour of the binary systems being considered. Then by using the known thermodynamic relations (1) and (2):

$$(\partial \ln f_2/\partial N_2)_{P,T,K} = 0, \quad (1)$$

$$(\partial^2 \ln f_2/\partial N_2^2)_{P,T,K} = 0, \quad (2)$$

where f_2 is the volatility of a component, N_2 its mole fraction, and K the critical phase, the pressure and composition of the critical point can be calculated. However, such an equation does not exist and, as Rakovskii noted[60], "the enormous power of the apparatus of thermodynamics stumbles about our ignorance of the actual equations of state"§.

Such a calculation could also be carried out if we had experimental data about the variation of the volume of the gaseous solution and of the components of the mixture with pressure and composition at different temperatures. Then, by calculating the volatility of a component of the solution a graph can be constructed in coordinates of $\ln f_2$ against N_2. The existence on such a graph of a point of inflection with a horizontal tangent (see, for example, Tsiklis and coworkers[61]) signifies that there is a region of layering in the system.

Usually such data are not available in the literature, and it is more difficult experimentally to obtain them than to make a direct investigation of the phase equilibria in the system.

The literature shows that attempts have been made to judge the possibility of the appearance in a given system of a region of gas–gas layering by comparing the properties of the components of the system. Mixtures should show layering when their components have not so much strong intermolecular interaction, as different.

Thus, Kreglewski[62] used the Hildebrand solubility parameter (Δ) and showed that the greater the difference between the value of Δ^2 of the components of the mixture the more probable the layering of the mixture. The solubility parameter is determined by the expression

$$\Delta = -(E/v)^{1/2} \quad (3)$$

where E is the energy of the component and v the molar volume. According to van Dranen's hypothesis[64], at the critical point the negative potential energy of a substance is $E = \frac{3}{2}RT_c$. Consequently, relation (4) holds for the critical point:

$$\Delta^2 = {}^3/_2 \frac{RT_c}{v_c}. \quad (4)$$

Table 2 gives values of Δ^2 for the components of the mixtures investigated and shows that in reality in all the mixtures which show layering the difference in the values

§ Schäfer[63] attempted to use for this purpose an equation of state with virial coefficients. By finding the values of these coefficients, Schäfer calculated by a very complex path the conditions of layering in the N_2–NH_3 system and obtained good agreement with experiment.

TABLE 2. Values of Δ^2 of the components of the mixtures investigated.

Component	T_c, °K	v_c, cm³ mole⁻¹	$(\Delta)^2$, at	Component	T_c, °K	v_c, cm³ mole⁻¹	$(\Delta)^2$, at
He	5.23	57.7	11.2	C_2H_6	526.1	260.0	266.4
H_2	33.25	65.7	63.2	C_2H_4	283.1	124.0	381.0
N_2	126.0	90.3	172.0	CO_2	304.1	93.3	399.0
C_4H_{10}	425.8	58.0	204.0	SO_2	430.4	123.7	228.0
C_5H_{12}	507.8	283.0	221.0	CH_3OH	513.0	129.0	490.0
C_3H_8	370.6	200.0	227.0	NH_3	406.1	72.9	685.0
CH_4	190.7	99.0	237.0	H_2O	647.0	54.7	1460.0
Ar	150.7	75.5	246.7				

of Δ^2 of the components is significant. Nevertheless, Kreglevskii's criterion is approximate. It does not allow a quantitative estimation of the parameters of layering to be given. Moreover, in a series of instances the calculation leads to erroneous results. For example, for the ammonia–hydrogen system the difference in the values of Δ^2 for ammonia and hydrogen is greater than in the ammonia–nitrogen system, but layering does not occur in the ammonia–hydrogen system.

Temkin[65] proposed a strict criterion of layering. By using the van der Waals equation of state for a binary mixture and the Helmholtz equation for free energy, he found the conditions for the development of the so-called longitudinal fold on the surface in the coordinates free energy–volume–composition, which, in accordance with the theory of folds[41], is also the condition for the layering of the mixture.

For calculation according to this criterion it is necessary to find the value of the coefficients a_1 and a_2 of the equation of state for the pure components and a_{12} for the binary system. Layering in the system is possible if Eqn. (5) is fulfilled for a mixture of non-polar components¶ and Eqn. (6) for mixtures containing polar components:

$$a_1 < 0.053\, a_2 \qquad (5)$$

$$^1/_2(a_1 + a_2) - a_{12} > {}^8/_{27}\, a_2. \qquad (6)$$

From Eqns. (5) and (6) it is evident that layering is possible when for mixtures of non-polar components the quantity a_1 is significantly less than a_2 and for a mixture with polar components a_{12} is less than the half-sum of the values of a_1 and a_2. Calculation shows that all systems with helium should show layering. Experiment confirms the calculation. It appears that even mixtures of helium and xenon — two noble gases — show layering. The results for layering in systems which contain water also agree with calculation.

However, this criterion is also approximate, since it is based on the van der Waals equation of state and this, as is known, is only qualitative, since it does not describe fully the behaviour of a substance at high pressures.

The layering of a homogeneous system, including also a phase transformation of the gas–gas type, indeed serves as a touchstone for any statistical theory of the condensed state of a substance.

In the theory based on the use of a method of correlating functions, phase transformations are connected with the singularities of the integral equations for these functions. Attempts to connect the crystal–liquid phase transformation with the presence of branching points in the integral equation for a single-index unary distribution function appeared quite fruitful.

In Rott's works[66] the phase transformation of interest to us here is considered from the standpoint of the statistical theory of the conditions for distribution. In it the phase transformation is connected with the singularity of the configuration integral. The latter is directly extended also to the distribution function itself (in the present instance the so-called two-index correlation functions). This can be traced also to the reverse dependence. If the state of the homogeneous system cannot be realised, then the distribution functions corresponding to it, say the most minor E_{11}, should transform to zero, which transforms the configuration integral into infinity. Therefore a knowledge of even the minor distribution functions (for the binary system there are two such functions) allows the approximate condition for the phase transformation to be found without resort to calculation of the configuration integral itself.

Thus for dilute binary solutions a final evaluation is obtained which allows us to find whether the occurrence of layering of the gas–gas type is possible or impossible; the parameters of the molecular interaction are calculated during this.

The criterion for layering in the given instance is the parameter β, given by

$$\beta = \frac{3.31\,\frac{\epsilon}{k}\,\sigma^4}{Tr_0^4}, \qquad (7)$$

where r_0 is the radius of the molecular volume ($v = \frac{4}{3}\pi r_0^3$), ϵ and σ are the parameters of the Lennard–Jones potential, k is Boltzmann's constant, and T the temperature.

It appears that the nature of the change in β is approximately the same for many substances. At the critical temperature $\beta \simeq 4$–5, at the triple point $\beta \simeq 28$ for the liquid phase and 34 for the solid.

In calculating the parameter β for a two-component system values of T and r_0 for the less volatile component (subsequently, for water, as an example) must be inserted in the denominator of Eqn. (7) and values of ϵ and σ for the more volatile (non-polar component) in the numerator. In this the value of β for the case when gas–gas layering of the first type is possible in the neighbourhood of the critical point of the less volatile component should be greater than its value at the critical point (that is, 4–5).

From the experimental results it is evident that features of the phase equilibrium known previously as features of helium solutions (the presence of a characteristic horn on the pressure–mole fraction curves near the critical point of the less volatile component) are present also in other binary systems the components of which do not differ greatly in energetic respects. Such are also all the systems with water considered below. Table 3 gives the values of β for a series of binary systems (aqueous solutions) in the vicinity of the critical point of water (for all the systems shown the critical density of water is greater than the density of the dissolved component at its critical point).

Experiment confirms the calculations. The layering in the water–butane systems is of the first type. In the water–nitrogen and water–carbon dioxide systems gas–gas equilibria of the first type are not observed. Gas–gas equilibria of the second type are observed.

¶ In essence Eqn. (5) is the particular case of Eqn. (6) when it is assumed that $a_{12} = \sqrt{a_1 a_2}$.

TABLE 3. Values of β for systems containing water.

System	β	Layering of the first type	System	β	Layering of the first type
Butane–water	~21	possible	Methane–water	2.4	impossible
Benzene–water	~28	»	Ethane–water	7.3	»
Propane–water	~42	»	Nitrogen–water	2.0	»
Octane–water	~82	»	Carbon dioxide–water	4.0	»

Attempts to use the methods of the statistical theory of "free volume" for the calculation of layering have been made recently [19].

New results obtained comparatively recently which relate to systems consisting of helium and fluorine compounds do not fit into the framework of any of the theories mentioned.

According to the criteria of Kreglewski, of Temkin, and of Rott, these systems (He–$CClF_3$, He–CHF_3, He–$CH_2{=}CF_2$, and He–SF_6) ought to have a region of gas–gas equilibrium of the first type. Experiment showed that they did not possess such a region [20,34].

In addition to that, mixtures of helium with other fluorine compounds, for example, He–$C_2Br_2F_4$ (Freon-114B2), He–$CHClF_2$ (Freon-22), and He–CCl_2F_2 (Freon-12) behave normally [35,36].

Evidently there is something new and interesting here in the unusual behaviour of the gaseous solutions of fluorine compounds. It is known [51,59,67] that liquid solutions which contain hydrocarbons and their fluoro-derivatives are also distinguished by unusual behaviour.

From the experiments described it is clear that the existence or absence of a region of gas–gas equilibrium of the first type in mixtures of helium and fluorine compounds is connected with features of the structure of these compounds. Evidently a negative part in the existence of layering is played by the polarity of the C–F bond and the small size of the fluorine atom. The latter assumes the approach of helium and fluorine, which can lead to polarisation of the helium and the production of additional interaction, which is unfavourable for layering†.

With a decrease in the number of fluorine atoms in the molecule, owing to the introduction of chlorine, bromine, or hydrogen, layering is produced.

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The comparatively recently observed phenomenon of restricted mutual solubility of gases was for a long time regarded as exotic. It can be hoped that the material presented in this review will disperse these doubts.

Gas–gas equilibrium is a widespread phenomenon. It has its place in the series of phase equilibria. Not only investigators occupied with the study of phase equilibria, but also technologists should take this phenomenon into account. This must be done both now (since this equilibrium starts at pressures and temperatures which are usual for many technological processes of the chemical and petroleum industries) and especially in the future, when high pressures will come into chemistry on a full scale.

This phenomenon will undoubtedly be used to explain many facts by geochemists, who are concerned with the problems of the formation and migration of petroleum, and also by scientists dealing with hydrothermal syntheses within laboratories and with the observation of these processes in nature.

It cannot be doubted that the number of experimental studies concerned with gas–gas equilibrium will grow and accordingly will extend our knowledge of this new and interesting phenomenon.

† Ya. K. Syrkin brought this to our attention.

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NEWTONIAN VISCOSITY OF CONCENTRATED SOLUTIONS OF POLYMERS

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The factors which influence the irreversible flow of high-molecular compounds and of their concentrated solutions have attracted increasing attention in recent years because of their relevance to current problems in the technology of polymer fabrication. However, the study of viscoelastic properties in polymers is important not only as a route to formulating the scientific foundations of technology: it can also provide valuable information on the nature and on the rates of conformational changes in macromolecules and also on their mutual arrangement (i.e. on the structure of the polymer and of its solution[1]).

Studies of the rheological properties of concentrated solutions of polymers began in the 1930's, when it was shown[2-4] that the anomalous flow of polymer solutions (and of the polymers themselves) arises from the interplay of elastic (reversible) deformations and viscous (irreversible) flow. It was subsequently shown[5] that relaxation phenomena are associated with the elastic deformations. Thus, concentrated polymer solutions give rise to a viscoelastic system: to investigate these solutions we must separate reversible from irreversible deformations, and also examine the rate of shear as a function of stress over a wide range of these parameters.

For polymer solutions of intermediate concentration this function gives, when plotted on logarithmic coordinates, a characteristic S-shaped curve with linear lower and upper sections at 45° to the horizontal axis[6] (Fig. 1).

Over these sections of the plot (i.e. in the regions of small or large shear rates or stresses) the viscosity coefficient is constant and the flow is Newtonian. The viscosities corresponding to the two linear sections are usually termed the maximum and the minimum Newtonian viscosity. It should be noted that with very concentrated solutions of high polymers, and with melts, the upper linear section (Fig. 1) is not observed: hence, most of the published values for the maximum Newtonian viscosity have been measured at insufficiently high stresses and shear rates. However, in many systems the viscosity depends on the applied shear stress even under these conditions, as can most clearly be seen by plotting the logarithm of the viscosity against the logarithm of the stress[7]. In this case the Newtonian viscosity is obtained by extrapolation to zero stress or to zero shear rate.

Low stresses cannot break down the structures present in melts or in solutions: hence, the Newtonian viscosity at low shear rates describes the flow of the solution without any disturbance of its structure. In this sense, studies of the Newtonian viscosity of polymer solutions are a very

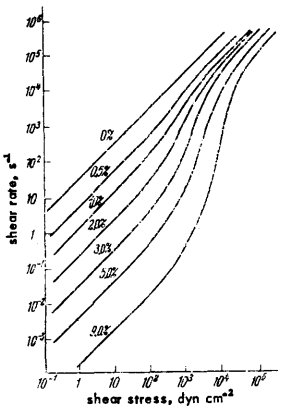


Fig. 1. Flow curves for solutions of polyisobutylene in decalin[6]. The numbers by the curves denote solution concentration.

important method of characterising their structure, particularly since direct structural examination of the solution (e.g. by electron microscopy) presents serious difficulty. At the same time, an extensive investigation by Vinogradov and coworkers[8,9] has shown that the maximum Newtonian viscosity has a fundamental significance, since it can be used as a normalising factor for a number of rheological characteristics.

Studies of the maximum Newtonian viscosity indicate that the flow mechanism of polymers and of their concentrated solutions is a general one. Hence it may be desirable to review briefly the main experimental and theoretical advances in the study of the viscosity of these polymers. Recent progress in this field is due mainly to the work of Kargin, Rebinder, Slominskii, Bartenev, Vinogradov, Trapeznikov, Ferry, Flory, Fox, Bueche, and others.

By generalising the large fund of experimental results obtained in recent years, two fundamental empirical relations have been derived, which relate the viscosity coefficient of a polymer (η) to the molecular weight (M)[10,11] and to temperature[12] respectively. Thus, for a large number of quite different polymers the plot of $\log\eta = f(\log M)$ consists of two intersecting straight lines whose point of intersection corresponds to a critical value of the molecular weight, M_c. Polymers for which $M > M_c$ obey the equation

$$\log\eta = 3.4\log Z + C, \qquad (1)$$

where Z is the degree of polymerisation and C is a constant. The second universal relation, known as the Williams, Landel, and Ferry (WLF) equation[12], states that the temperature dependence of the viscosity of polymeric substances can also be described by a universal empirical equation:

$$\log a_T = \log\frac{\eta_T \rho_S T_S}{\eta_S \rho_T T} = -\frac{C_1^0 (T - T_S)}{C_2^0 + T - T_S}, \qquad (2)$$

where η_T and ρ_T are the viscosity and the density of the polymer at the given temperature T, whilst η_S and ρ_S are the viscosity and the density of the polymer at the standard temperature T_S (reference temperature), chosen so as to make the plots of $\log a_T = f(T - T_S)$ for the different polymers coincide; C_1^0 and C_2^0 are coefficients dependent on the nature of the polymer and on the reference temperature. For polyisobutylene $T_S = 243°K$, $C_1^0 = 8.86$, and $C_2^0 = 101.6$. For other systems these coefficients are retained and the reference temperature is varied.

Eqn. (2) is applicable over the temperature range from the glass transition temperature T_g to $T_g + 100°$. Under these conditions the ratio $\rho_S T_S/\rho_T T$ is close to unity. Hence $\log a_T \simeq \log \eta_T/\eta_S$.

If the reference temperature is defined as the glass transition temperature of the experimental material, Eqn. (2) becomes universally applicable to polymers and low-molecular glass-forming liquids:

$$\log a_T = \log\frac{\eta}{\eta_g} = -\frac{17.44\,(T - T_g)}{51.6 + T - T_g}, \qquad (3)$$

where η_g is the viscosity at the glass transition temperature.

The glass point is the most convenient reference temperature because it can be determined for each polymer by an independent method, but measurements of viscosity and other mechanical properties are difficult to make in the neighbourhood of T_g. A temperature approximately 50° higher than the glass point is therefore commonly used: $T_S = T_g + 50°$.

Eqn. (2) is a particular case of the temperature dependence of any viscoelastic property, and demonstrates the principle of temperature–time superposition first formulated for polymers by Aleksandrov and Lazurkin[5]. Essentially, the principle states that temperature and the time of application (frequency) of a force play identical roles because the deformation shows a relaxation behaviour. Therefore, plots of the property against temperature can be mutually superimposed by shifting them along the temperature axis. This means that the ratio of the relaxation times (τ_r) at two temperatures is a constant:

$$\frac{(\tau_r)_T}{(\tau_r)_{T_S}} = a_T = \frac{\eta \rho_S T_S}{\eta_S \rho T}.$$

Thus, the Newtonian viscosity is directly related to the relaxation time of the system.

Eqns. (1) and (2) can also be derived theoretically, starting from the fundamental postulates of the theory of the viscous flow of liquids and polymers.

Since liquids occupy a position intermediate between gases and solids, the liquid state has been treated from the point of view of both these states. At the turn of the century liquids were discussed by analogy with gases. X-Ray diffraction studies of simple liquids revealed the existence of ordered regions and gave rise to the hypothesis of a quasi-crystalline liquid structure. In reality, the liquid state is qualitatively different from the others, and can be described by means of the radial density distribution function[13].

Contemporary statistical theories of the liquid state are of two kinds: (a) the more accurate and more complicated theories based on studies of molecular distribution functions, and (b) the less accurate but simpler "lattice" theories or "free volume" theories, based on the concept of a quasi-crystalline liquid structure.

The idea of "free volume" in a liquid is not entirely unequivocal. Thus, in the statistical theory of liquids this term denotes a complex integral which can be evaluated to give a "mean" volume within which the "average" molecule is able to move freely at a given temperature. This "free volume" does not actually exist in a liquid: it is a fictitious

quantity which appears in statistical calculations as a result of the particular method of approximation used[13]. Yet, a number of workers have attempted to ascribe a physical significance to this term. Most of them interpret liquid free volume as empty regions between molecules, i.e. as voids or "holes" of molecular (monomer) dimensions arising from irregularities in packing[1]. Frenkel'[14] showed by thermodynamic arguments that molecular voids (vacancies) can exist also in real crystals. However, the free volume in crystals is different in nature from the free volume in liquids. Crystal free volume is due to asymmetry in the vibrations of the particles, and its distribution among the particles is continuous (Fig. 2*a*). This is the so-called vibrational volume. Liquid free volume consists of two parts: 1) a continuous part, also associated with the vibrations of the particles in the liquid, and 2) a discrete part, due to voids (Fig. 2*b*). The latter enables the particles to undergo continuous place exchange, i.e. the "holes" in a liquid are fluctuating entities[14,15].

The free volume of a substance is difficult to measure. Most commonly, the free volume v_f of a liquid or a crystal is determined as the difference between the specific volume of the material at the given temperature (v_{sp}) and at the absolute zero (v_0), the latter being obtained by extrapolating to $T \to 0$ the linear plot of $v_{sp} = f(T)$ (Fig. 3):

$$v_f = v_{SP} - v_0. \tag{4}$$

As the free volume increases, the specific volume of the liquid also increases: the major contribution to the thermal expansion coefficient of a liquid is the increase of free volume with increase of temperature.

The internal friction of liquids depends on the free volume, since relative movement of the molecules is made possible by the presence of free space between the molecules. This relation was first pointed out by Bachinskii[16], who proposed the equation

$$\eta = \frac{C}{v - w}, \tag{5}$$

where v is the specific volume of the liquid and w is the arithmetic mean of the volumes of 1 g of the liquid at the given temperature and at the freezing point. The difference $v - w$ was termed the "free" volume. If we write Eqn. (5) in the form

$$v = w + \frac{C}{\eta} \tag{6}$$

it is obvious that the plot of $v = f(1/\eta)$ at any given temperature should be a straight line not passing through the origin: this was confirmed for 66 different liquids. Associated liquids do not obey Eqn. (6).

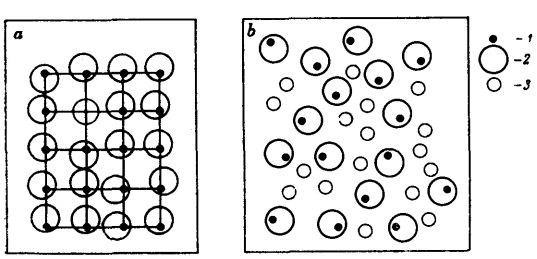


Fig. 2. Schematic representation of free volume[15]: (*a*) crystal; (*b*) liquid; 1) molecules, 2) vibrational volume of molecules, 3) "holes".

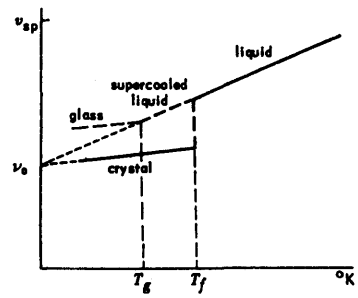


Fig. 3. $v-T$ diagram for a substance in the condensed phase.[15]

More recently, Doolittle[17] proposed another empirical equation for the viscosity of a liquid:

$$\ln \eta = \ln A + B\frac{v_0}{v_f}, \tag{7}$$

where v_0 and v_f are the occupied and the free volume respectively.

Eqn. (7) may be written in the form

$$\eta = A\, e^{Bv_0/v_f}. \tag{8}$$

It is interesting to note that the temperature does not appear explicitly in Eqns. (5) and (7). This is one of the most fundamental aspects of the modern theory of viscous flow, which is treated as a process made up of the activated jumps of individual elementary units of flow from one equilibrium position to another. The jumping frequency is controlled by the height of a potential barrier, and is denoted by the symbol I.

The activation theory of liquid flow, proposed by Frenkel'[14] and developed by Eyring and others[18], leads to the following expression for the temperature dependence of viscosity:

$$\eta = \frac{N_A h}{V} e^{\Delta G_{visc}/RT}, \tag{9}$$

where V is the molar volume of the liquid, ΔG_{visc} is the free energy of activation of the viscous flow of one mole of molecules passing from one equilibrium position to another. If we write $\Delta G_{visc} = \Delta H_{visc} - T\Delta S_{visc}$, Eqn. (9) takes the form

$$\eta = \frac{N_A h}{V} e^{\frac{-\Delta S_{visc}}{R}} e^{\frac{\Delta H_{visc}}{RT}} \tag{10}$$

The plot of $\log \eta = f(1/T)$ is thus a straight line whose slope is a measure of the quantity ΔH_{visc}, the heat of activation of the viscous flow. This quantity is determined by the temperature coefficient of viscosity. ΔS_{visc} is the entropy of activation of the viscous flow.

Experimental observations have shown that Eqns. (9) and (10) apply only over a narrow range of temperatures. Over a wider temperature interval the plot of $\log \eta = f(1/T)$ is curvilinear, and Kobeko suggests that the curvature of this plot is a characteristic of the liquid state[19]. From plots of this type one calculates the so-called apparent heat of activation of viscous flow:

$$\Delta H_{visc} = \frac{d \ln \eta}{R\, d\,(1/T)}, \tag{11}$$

which is itself a function of temperature. It can be shown theoretically that the heat of activation of viscous flow is

related to the temperature coefficient of the molecular jumping frequency I and also to the temperature coefficient of the free volume [20]:

$$\Delta H_{visc} = -R\left[\frac{\partial \ln I}{\partial (1/T)}\right]_{v_f} - R\left(\frac{\partial \ln I}{\partial v_f}\right)\left[\frac{\partial v_f}{\partial (1/T)}\right]. \quad (12)$$

Thus, the decrease of liquid viscosity with increase of temperature stems from two distinct causes: 1) the increase in jumping frequency and 2) the increase in free volume.

All these conclusions of the theory of the viscous flow of liquids are used in discussions of polymer flow. It is assumed that the elementary unit of flow is a portion (or segment) of the polymer chain rather than the entire chain. Chain segments are interconnected by valence bonds, and they interact with the segments of neighbouring chains, so that their motions are not mutually independent. The viscosity of the polymer is given as the product of two quantities: a function of the chain length $F(Z)$ and the reciprocal of the jumping frequency I:

$$\eta = \frac{F(Z)}{I}. \quad (13)$$

The form of the function $F(Z)$ is the same for all polymers: it allows for the interaction between units, and is independent of temperature. The jumping frequency depends both on temperature and on the local disposition of the units (i.e. on the free volume). The greater the free volume, the greater are the specific volume and the jumping frequency I, and the lower is the viscosity of the liquid or polymer [20].

Free volume considerations have proved very fruitful in bringing about an understanding of the viscous flow of polymers. Thus, it became clear that the quantity a_T in the WLF Eqn. (2) is related to the free volume of the polymer, and that the equation itself can be deduced theoretically from Doolittle's equation [1,12]. The expression obtained is indistinguishable from the WLF equation if the fractional free volume at the glass point is taken as $f = 0.025$, and the thermal expansion coefficient as $\alpha = 4.8 \times 10^{-4}$ deg^{-1}.

Bueche [21,22] also used free volume considerations, and proposed that the resistance to flow of a polymer arises from: (1) friction of the segments of the polymer chain as it moves relatively to its neighbours; (2) interaction between the segments joined by primary valence bonds into a long chain; (3) interlocking of the chains with formation of a network structure. If the chain consists of N monomer units and ζ_0 is the molecular (monomeric) friction factor, related to I (the number of jumps of the unit) and to δ (the average change in the position of its centre of gravity) by the expression

$$\zeta_0 = \frac{6kT}{I\delta^2}; \quad (14)$$

the viscosity coefficient is given by

$$\eta = FN\zeta_0, \quad (15)$$

where the proportionality coefficient F depends on the molecular weight of the polymer.

When $M > M_c$ (see p. 362)

$$\eta = k'M\rho\zeta_0; \quad (16)$$

when $M < M_c$

$$\eta = kM^{3.5}\rho^4\zeta_0 \quad (17)$$

where ρ is the density of the polymer, k' and k are constants.

I. CONCENTRATED SOLUTIONS OF POLYMERS

The term concentrated usually denotes solutions in which the solute molecules can interact with each other. In polymer solutions interactions of this type give rise to a steep increase in viscosity as compared with the viscosity of the pure solvent. Ferry [1] proposed that polymer solutions should be called concentrated if their relative viscosity is of the order of 100 or more. The lower concentration limit of the polymer can vary from 1% (for unusually long, rigid chains) to 10% (for flexible polymers of low molecular weight). The upper limit is the undiluted polymer.

Studies over a wide range of concentration, temperature, polymer chain length, and solvent type can lead to significant advances in establishing the relationships which govern the viscosity of concentrated polymer solutions.

1. Effect of Concentration

Up to the year 1960 our understanding of the isothermal concentration dependence of the viscosity of polymer solutions was limited, because most of the data then available related to a narrow concentration range. Thus, owing to experimental difficulties, most of the workers studied the viscosity of polymer solutions in the concentration range up to 0.2 [23-46] or 0.5 [47-52] weight fraction of the polymer.

Far fewer papers have dealt with the viscosity of solutions over the whole or most of the concentration range [53-58], but in recent years such papers have appeared in increasing numbers [60-69].

The viscosity of a solution varies with concentration as shown by the curves of Fig. 4. For solutions of polymers of fairly high molecular weight, and at low concentrations of the polymer, the curve is convex towards the ordinate axis. On further increasing the concentration the viscosity increases more slowly. A steeper rise sets in again when very concentrated polymer solutions are held near the glass point of the polymer. This effect is due to the rapid decrease of the relative free volume [70].

There have been repeated attempts to establish analytically the relation between the viscosity and the concentration of the solution. Thus, Flory [54] studied the viscosity

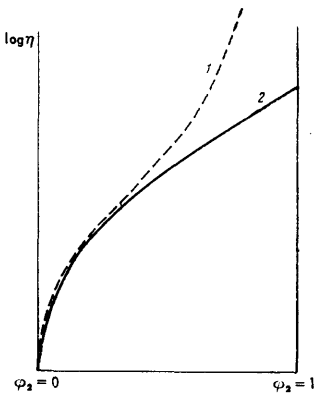


Fig. 4. Variation of solution viscosity with concentration:
1) solutions of glassy polymers; 2) solutions of elastic polymers.

of solutions of poly(decamethylene adipate) over the entire composition range from pure solvent to the pure polymer, and showed that above 0.1 weight fraction of the polymer the viscosity varies with concentration according to the equation

$$\log\eta = A + B\omega_2^{1/2} \quad (18)$$

where ω_2 is the weight fraction of dissolved polymer, and A and B are constants. Eqn. (18) can be obtained from the equation relating the viscosity of a polymer melt to its molecular weight[71] by treating the solvent molecules as short polymer chains. Hence it was concluded that the mechanism of flow of concentrated polymer solutions is analogous to that of the polymers themselves: in the flow of concentrated solutions also the polymeric chains move as a result of the motion of their individual segments. Eqn. (18) was confirmed experimentally by the work of Spencer and Williams[47] on the viscosity of polystyrene solutions in the concentration range between 0 and 0.5, and also by an investigation[25] of the viscosity of butadiene–styrene rubber solutions in the concentration range between 0.10 and 0.19 weight fraction of the polymer. It was not confirmed, however, over a wider range of concentrations[48-51] for solutions of poly(vinyl acetate), polyisobutylene, and polystyrene.

Attempts were made to apply to the flow of concentrated polymer solutions the equation derived by Martin for the flow of dilute solutions of polymers[26,47]:

$$\log\frac{\eta_{sp}}{C} = \log[\eta] + K[\eta]C \quad (19)$$

where C is the concentration, $[\eta]$ is the characteristic viscosity, and K is a constant.

It follows from the reported measurements that Eqn. (19) satisfactorily describes the experimental results of the authors only if the concentration does not exceed 0.12 weight fraction of the polymer.

All the equations given above are empirical. There are now a number of theoretical equations for the concentration dependence of the viscosity of polymer solutions, derived on the basis of the fundamental concepts discussed above and on the assumption that dilution decreases the relaxation times of the system and the monomer friction coefficients.

In a solution, each monomer unit of a polymer chain is surrounded both by the units of neighbouring chains and by solvent molecules, the latter being able to move much more readily than the former. Hence, introducing small molecules whose motion (unlike that of the segments of molecular chains) immediately produces irreversible structural changes is enough to raise the fluidity, i.e. to lower the viscosity of the system[72].

The theoretical interpretation of the dilution of a polymer system is usually that the decrease in viscosity stems from the increase in free volume brought about by the introduction of the solvent. The following arguments are generally used: (1) the free volume of the solvent is greater than that of the polymer; (2) the volume of the solution is an additive function of the volumes of the components; (3) the free volume of the solution is the sum of the free volumes of the components:

$$v = v_1 + v_2 \quad (20)$$

where v, v_1, and v_2 are the volumes of the solution, the solvent, and the polymer respectively, and

$$v_f = (v_f)_1 + (v_f)_2 \quad (21)$$

where v_f, $(v_f)_2$ are the mean free volumes of the solution and the polymer (at the same temperature), and $(v_f)_1$ is the newly formed free volume resulting from the addition of solvent. Two attempts to derive the concentration dependence of the viscosity of polymer solutions have been reported. The first is due to Fujita and Kishimoto[73], who assumed that $(v_f)_1$ increases when the volume of solvent is increased, but is also a function of concentration and of temperature. If $(v_f)_1$ is assumed to be a function of temperature only, Eqn. (21) takes the form

$$v_f = (v_f)_2 + \gamma(T)v_1, \quad (22)$$

where $\gamma(T)$ is a function which characterises the particular polymer–solvent system.

Dividing Eqn. (22) by Eqn. (20) we obtain an expression for the relative free volume of the solution:

$$f = \frac{v_f}{v} = \frac{(v_f)_2}{v_2} + \left[\gamma(T) - \frac{(v_f)_2}{v_2}\right]\varphi_1, \quad (23)$$

where φ_1 is the volume fraction of solvent in the solution.

The ratio $(v_f)_2/v_2$ is the relative free volume of the polymer at temperature T, and it can be expressed in the form $f(T, 0)$ at $\varphi_1 = 0$ if the free volume of the solution is described by the function $f(T, \varphi_1)$. Eqn. (23) can then be written

$$f(T, \varphi_1) = f(T, 0) + \beta'(T)\varphi_1, \quad (24)$$

where

$$\beta'(T) = \gamma(T) - f(T, 0). \quad (25)$$

Using Eqns. (7) and (8) for T = const, the authors arrive at an expression of the form

$$-\frac{1}{\ln a_C} = f(T, \varphi_1^*) + \frac{f(T, \varphi_1^*)}{\beta'(T)}\cdot\frac{1}{\varphi_1 - \varphi_1^*} \quad (26)$$

$$a_C = \frac{\eta(T, \varphi_1)(1 - \varphi_1^*)}{\eta(T, \varphi_1^*)(1 - \varphi_1)}, \quad (26a)$$

where $\eta(T, \varphi_1)$ and $\eta(T, \varphi_1^*)$ are the viscosity coefficients of solutions for which the volume fractions of the first component are φ_1 and φ_1^* (chosen as a standard solution), $f(T, \varphi_1^*)$ is the free volume of the solution of standard concentration, and $\beta'(T)$ is a function which can be calculated from Eqn. (25).

It follows from Eqn. (26) that the plot of $\frac{1}{\ln a_C} = f\left(\frac{1}{\varphi_1 - \varphi_1^*}\right)$ should be a straight line whose slope is a measure of $\beta'(T)$ and whose intercept on the ordinate axis gives the value of $f(T, \varphi_1^*)$. The standard state can be defined as a solution of any arbitrary concentration, or the pure polymer.

The authors tested their equation with the following systems: polystyrene–diethylbenzene[56], polystyrene–dibenzyl ether[20], polystyrene–decalin[51], poly(methyl methacrylate)–diethyl phthalate[58], and poly(methyl acrylate)–diethyl phthalate[66].

Eqn. (26) holds for very concentrated solutions, and departures from linearity are observed when $\varphi_1 > 0.5$. The slope of the straight line increases with temperature, i.e. the quantity $\beta'(T)$ varies, and therefore also $\gamma(T)$, which (as was to be expected) has different values for different systems. The function $f(T, 0)$, i.e. the relative free volume of the polymer itself, calculated from the intercept of the straight line on the ordinate axis, is constant for a given polymer. Its temperature dependence can be approximated by two straight lines intersecting at the glass point of the polymer. Quantities calculated from Eqn. (26) for the polystyrene–ethylbenzene[65] and polyisobutylene–toluene[64]

systems are plotted in Fig. 5. Minor departures from linearity can be observed for the first system at $\varphi_1 > 0.5$, whereas for the second system Eqn. (26) is obeyed over practically the whole of the concentration range.

The second attempt to derive a theoretical equation for the concentration dependence of the viscosity of a polymer solution is due to Kelley and Bueche[74], and is based on similar premises. The authors express the relative free volume of the polymer and of the solution at a given temperature T in the form

$$v_{f_2}/v_2 = 0.025 + 4.8 \times 10^{-4}(T - T_g). \quad (27)$$

and

$$v_{f_1}/v_1 = 0.025 + \alpha_S(T - T_g') \quad (27a)$$

where 0.025 is the relative free volume of the material at T_g; 4.8×10^{-4} deg^{-1} is the temperature coefficient of the relative free volume of the polymer (see p. 364); α_S is the temperature coefficient of the relative free volume of the solvent, which for liquids is of the order of 10^{-3} deg^{-1}, T_g and T_g' are the glass points of the polymer and the solvent respectively. Assuming additivity of the free volumes, the following expression is obtained for the relative free volume of the solution:

$$v_f/v = \varphi_2[0.025 + 4.8 \times 10^{-4}(T - T_g)] + (1 - \varphi_2)[0.025 + \alpha_S(T - T_g')]. \quad (28)$$

Using Eqns. (8) and (17) the authors arrive at an expression for the viscosity of the solution:

$$\log \eta/B = 4 \log \rho[\varphi_2[0.025 + 4.8 \times 10^{-4}(T - T_g)] + (1 - \varphi_2)[0.025 + \alpha_S(T - T_g')]]^{-4}, \quad (29)$$

where ρ is the density or concentration by weight of the polymer in solution, φ_1 and φ_2 are the volume fractions of the solvent and of the polymer, η is the viscosity of the solution, and B is a parameter which includes the molecular weight of the polymer.

The authors tested the validity of Eqn. (29) on the following systems: polystyrene–diethylbenzene[56], poly(methyl methacrylate)–diethyl phthalate[57], and polyisobutylene–xylene[50]. For the first of these systems, taking T_g' = = -110°, good agreement was found between theory and experiment. The agreement was good also for the third system at 25° (T_g' = -50°) and for the second system at 120° and 140° (T_g' = -65°). At 60° the second system showed significant discrepancies between theory and experiment.

Calculated and experimental data for the polystyrene–ethylbenzene, polystyrene–decalin[65], and polyisobutylene–toluene[64] systems are reproduced in Fig. 6. The experimental points for the latter system lie on the theoretical

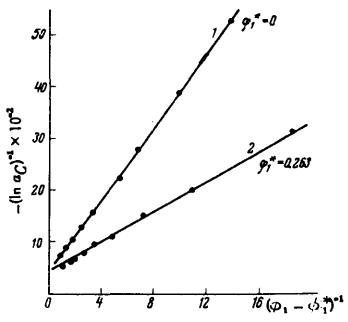


Fig. 5. Plot of $\ln a_C = f(\varphi_1)$ at 20°: 1) polyisobutylene–toluene; 2) polystyrene–ethylbenzene.

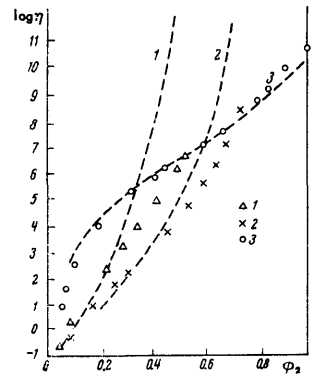


Fig. 6. Variation of viscosity with volume fraction of the polymer in solution at 20°: 1) polystyrene–decalin; 2) polystyrene–ethylbenzene; 3) polyisobutylene–toluene. The broken curves were calculated theoretically using Eqn. (29).

curve, whereas for the first two systems the theoretical and the experimental curves do not coincide.

The better agreement between theory and experiment at temperatures above the glass point of the polymer itself is striking, and cannot be fortuitous. It arises from the fact that the packing density of the macromolecules of polymers in the elastic state is very close to that of molecules of their low-molecular-weight analogues[75]. Hence there is practically no contraction when polymers such as polyisobutylene are mixed with iso-octane or other similar liquids of low molecular weight[76]. In systems of this type the principle of additivity of free volumes, which underlies the theoretical treatments, is valid to a first approximation. But it is very doubtful whether this principle can be applied to solutions of glassy polymers, particularly those which are loosely packed, and which undergo considerable contraction on dissolution[76]. Also, Eqns. (27) are evidently generally applicable only at temperatures above T_g for the polymer[1].

2. Variation of the Viscosity of Solutions with the Molecular Weight of the Dissolved Polymer

The early investigations of the viscosity of concentrated polymer solutions were made over a narrow range of molecular weights of the polymer: from 8.6×10^4 to 1.0×10^5,[47] or from 0.32×10^6 to 1.10×10^6.[50] Under these conditions Ferry showed that the viscosity of the solutions varied as the 3.4th power of the molecular weight of the polyisobutylene.

Bueche's papers describe a detailed study of the influence of the molecular weight of polymers on the viscosity of their concentrated solutions. This worker examined 15 polystyrene fractions (molecular weights between 5.0×10^4 and 10×10^6 [56]) and 14 fractions of poly(methyl methacrylate) covering molecular weights from 5.0×10^3 to 5.0×10^6,[57] at two concentration levels and one concentration level respectively. He showed that the variation of the logarithm of viscosity with the logarithm of chain length for a polystyrene solution of concentration 0.44 and a poly(methyl methacrylate) solution of concentration 0.25 weight fraction of the polymer is expressed, as in the case of the polymer itself,

by two intersecting straight lines. The lines corresponding to the longer chains are steeper and all have the same slope of 3.4, i.e. they are described by Eqn. (1). It was subsequently found that the viscosity data for solutions of polyacrylonitrile [44,46] and poly(vinyl alcohol) [29,33] are also described by this equation. The variation of viscosity with chain length of the dissolved polymer was established over wide concentration limits in the work of Porter and Johnson [59,77] and of Tager and coworkers [63]. Fig. 7 shows the results obtained for solutions of 7 samples of polyisobutylene of molecular weight between 0.9×10^3 and 1.2×10^6. It is obvious from the figure that in the concentration range which was investigated (from 0.05 volume fraction of the polymer upwards) the variation is described by two intersecting straight lines. The slope of the lines corresponding to the higher values of molecular weight is independent of the concentration of the solution, but the slope of the left-hand branches (corresponding to low molecular weights) increases with concentration. The slope of the right-hand branches is 3.4, i.e. these lines obey Eqn. (1). In agreement with Bueche's theoretical predictions [56] (p. 364) and with his data for polystyrene solutions, both the straight lines and their points of intersection are shifted towards larger Z values by decreasing the concentration of the polyisobutylene solution. However, the product of the critical chain length Z_C (given by the intersection of the straight lines) and of the concentration of the solution remains approximately constant (see Table).

The value of the product of critical chain length and concentration depends on the nature of the dissolved polymer: the more rigid the polymer chain, the lower is $Z_C\varphi_2$. Thus, values of 180 and 80 have been reported for solutions of polyisobutylene [63,69] and of poly(vinyl alcohol) [33] respectively. The same investigations reveal that Z_C varies with temperature and that increase of temperature causes a slight increase in the value of $Z_C\varphi_2$.

Ferry and coworkers [51,52] found that the viscosity of solutions of polyisobutylene, cellulose trinitrate, and cellulose tributyrate, when referred to the viscosity of the solvent, is a unique function of the product $Z^{3.4}\varphi_2^5$: the curves

TABLE. Product of the critical chain length Z_C and of the volume fraction of the polymer φ_2 for polyisobutylene solutions in iso-octane at 20°. [69]

φ_2	$Z_C\varphi_2$	φ_2	$Z_C\varphi_2$
0.05	140	0.30	210
0.10	160	0.40	200
0.15	150	0.50	180
0.20	140		

for solutions of all three polymers coincide. This relationship was shown to be valid also for solutions of poly(vinyl alcohol) [33]. However, the authors themselves point out that the expression does not apply at high concentrations [51]. Tests of the expression over a wide range of concentrations and molecular weights of dissolved polymer, using solutions of polyisobutylene [69] and poly(methyl methacrylate) [66], showed that the expression does not hold.

3. Effect of Temperature on the Viscosity of Polymer Solutions

Most investigations of the viscosity of concentrated polymer solutions have been confined to a fairly narrow temperature interval of 40–60° [25,27,28,36,37,47–51,62–65,78,79], and only a few studies [56,57,66–68] have dealt with temperature changes of 100–200°. The results indicate that over a 40–60° temperature interval the logarithm of the viscosity varies linearly with reciprocal temperature, but over a wider range of temperatures non-linearity sets in, and the curvature increases with the concentration of the solution (Fig. 8).

As we have already pointed out, curvature in the plot of $\log\eta = f(1/T)$ is associated with the nature of the liquid state [19]. A similar variation of the logarithm of the viscosity is found with low-molecular liquids, their solutions, and polymer melts and solutions. Measurements of specific heat, mechanical properties, volume changes, and viscosity indicate that the molecules of a multicomponent liquid form a single continuous system [19].

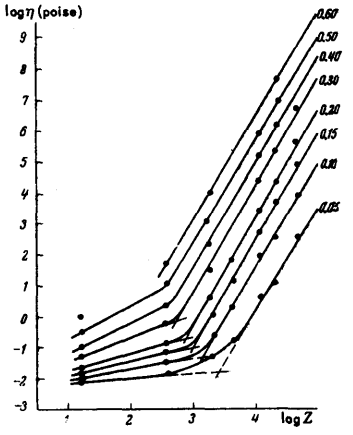


Fig. 7. Variation of the viscosity of polyisobutylene solutions in iso-octane with degree of polymerisation of the polymer [63]. The numbers by the straight lines denote the volume fraction of polyisobutylene in solution.

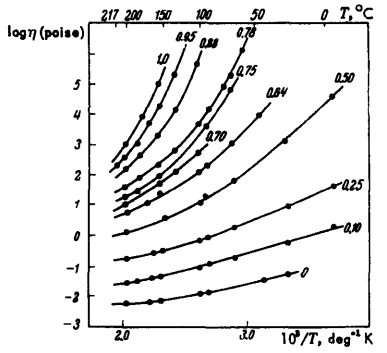


Fig. 8. Temperature dependence of the viscosity of polystyrene solutions in dibenzyl ether [20]. The numbers by the curves denote the weight fraction of the polymer in solution.

A concentrated solution of a polymer is also a single continuous system, differing from the polymer itself by having shorter relaxation times. Since the nearest neighbours of the polymer segments are solvent molecules, mutual friction takes place, and the jumps of segments and small molecules alike require a definite activation energy. Hence the term "energy" or "heat of activation" can be applied to concentrated solutions of polymers just as it can to the polymers themselves. (Very dilute solutions of polymers are an exception, and involve a radically different friction mechanism[80].) These terms are applied to concentrated solutions of polymers[48,52,56,57] and to plasticised systems[72].

The heat of activation for viscous flow depends on the concentration of the solution. It increases with increasing volume fraction of the polymer: linearly over a relatively narrow concentration range (from $\varphi_2 = 0.05$ to $\varphi_2 = 0.5$)[27,28,36,37,47,49] and non-linearly over a wider range of compositions[56,57,62-65]. It can be seen from Fig. 9 that the heat of activation for flow rises most steeply at high concentrations for solutions of polymers close to the glassy state: at $\varphi_2 = 1$ (polymer), ΔH_{visc} is of the order of hundreds of kilocalories per mole.

The slope of the function $\log\eta = f(1/T)$ increases when the material (or the solution concentration) is changed because the intermolecular interaction energy increases[19], as a result (in the present case) of a decrease in the free volume, or of approaching the glass point of very concentrated solutions[70].

The heat of activation for the flow of a solution depends also on the molecular weight of the dissolved polymer: this was demonstrated for solutions of cellulose tributyrate[52] and of poly(vinyl alcohol)[33,46], which were investigated over the composition range up to $\omega_2 = 0.40$ and $\omega_2 = 0.25$ respectively. Measurements were made over the whole composition range and a wide range of molecular weights for solutions of polyisobutylene[63,77]: the results are shown in Fig. 10. For not too high concentrations ($\varphi_2 < 0.35$) the heat of activation increases with the molecular weight of the polymer; at concentrations $\varphi_2 > 0.35$ we find a sharp increase in ΔH_{visc} on going from $M = 10^2$ (iso-octane) to 0.9×10^3 (from 1.9 to 14.5 kcal mole^{-1}).

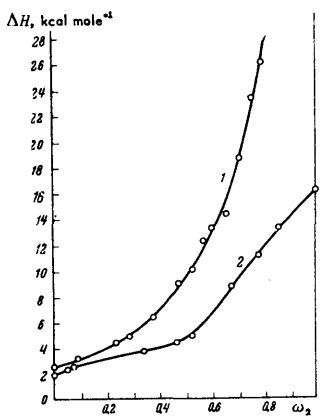


Fig. 9. Variation of the heat of activation for viscous flow with weight fraction of the polymer in solution:
1) polystyrene–diethylbenzene[56]; 2) polyisobutylene–toluene.[64]

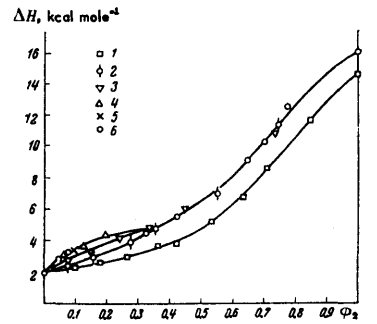


Fig. 10. Concentration dependence of the heats of activation for viscous flow of polyisobutylene solutions in iso-octane[63]:
1) $M = 0.9 \times 10^3$; 2) $M = 2.0 \times 10^4$; 3) $M = 1.1 \times 10^5$; 4) $M = 2.4 \times 10^5$; 5) $M = 6.5 \times 10^5$; 6) $M = 1.2 \times 10^6$.

Increasing the molecular weight of the polymer from 0.9×10^3 to 2×10^4 raises ΔH_{visc} by 1.6 kcal mole^{-1} (from 14.5 to 16.1). Further increase of molecular weight has no effect on the heat of activation for viscous flow.

The lack of dependence of the heat of activation for the flow of concentrated polymer solutions upon the molecular weight of the dissolved polymer, like the general validity of Eqn. (1), argues for a general mechanism of flow in polymers and their concentrated solutions. Hence we may suggest that other relationships, derived for the flow of polymers, should also be valid for solutions of polymers. Thus, Ferry[1] states that the temperature dependence of the viscosity of concentrated solutions of polystyrene, poly(vinyl chloride), poly(vinyl acetate), and cellulose tributyrate is satisfactorily described by the WLF equation.

A similar relationship was recently proposed[67] for polymer solutions: the equation obtained is

$$-\frac{T-T_0}{\log a_T} = \frac{[f(\varphi_1,T_0)]^2}{a_f(\varphi_1)} + (T-T_0)f(\varphi_1 T_0) \qquad (30)$$

where T and T_0 are the experimental and the reference temperature respectively; $f(\varphi_1, T_0)$ is the relative free volume of a solution of the given concentration φ_1 at the reference temperature T_0; $a_T = \eta(\varphi_1, T)/\eta(\varphi_1, T_0)$, and $af(\varphi_1)$ is a function of concentration. The plot of $-(T - T_0)/\log a_T = f(T)$ is a straight line whose slope measures $f(\varphi_1, T_0)$ and whose intercept on the ordinate axis measures $af(\varphi_1)$. The linearity of this function was confirmed in the poly(n-butyl methacrylate)–diethyl phthalate system.

4. Effect of the Nature of the Solvent on the Viscosity of Polymer Solutions

The effect of the nature of the solvent on the viscosity of concentrated solutions of polymers has been least thoroughly investigated, in spite of the essential relevance of intermolecular interaction and of its influence on all rheological properties. As already stated, the addition of small, readily mobile molecules to a polymer causes a dramatic increase in the fluidity and free volume of the system. Hence we can suggest that the addition of solvents and plasticisers to a polymer should affect the viscosity and all related properties in direct proportion to the volume fraction of the solvent and irrespectively of the nature of the solvent: the same conclusion follows also from a number of

theoretical equations. The earliest studies of the problem appeared to confirm this point of view. Thus, Ferry and coworkers[49-51] examined solutions of poly(vinyl acetate) in five solvents, of polyisobutylene in two solvents, and of polystyrene in two solvents up to weight fractions of the polymer of $\omega_2 = 0.5-0.6$, and showed that the viscosities are similar at a given volume fraction, but differ if the solutions are compared at a given weight fraction†.

The influence of the nature of the solvent on the viscosity of polymer solutions has been studied also by other workers[26,38,42,47,59], but either over a limited concentration range or over a limited range of solvents. A detailed study of the problem was made with solutions of polyisobutylene in six chemically different liquids, and of polystyrene in five liquids, over a wide range of compositions and at temperatures between 20° and 50°.[62,64,65,69] It was shown that even the viscosity of solutions of a polymer as elastic as polyisobutylene, whose chains contain only groups of a single type, depends on the nature of the solvent. The effect of solvent on the viscosity of polymer solutions is specially marked when the polymer is close to T_g under the conditions of the experiment. Thus, the viscosities of decalin and ethylbenzene solutions of atactic polystyrene at 20° and equal volume fractions differ by a factor of several hundreds.

With rise in temperature the concentration–viscosity curves of solutions in different solvents tend to coalesce, and at temperatures above T_g for polystyrene the viscosities of decalin and ethylbenzene solutions differ only by the viscosity difference between the solvents themselves.

The fall of viscosity with increase of temperature is not the same in solutions in different solvents: in other words, the heat of activation for viscous flow also depends on the nature of the solvent. It is important to note that the order of the plots of $\log\eta = f(C)$ and $\Delta H_{visc} = f(C)$ is the same, both for polyisobutylene and for polystyrene solutions. This suggests that the viscosity of concentrated solutions of polymers, like the viscosity of low-molecular liquids and their mixtures, is determined by the heat of activation for flow[19].

Several workers have suggested[26,42,49-51] that the viscosity of a polymer solution is controlled by the viscosity of the solvent. Thus, there is evidence[62,64,65,69] that the viscosity of the solution is highest in the most viscous solvent and lowest in the least viscous solvent. However, the viscosities of decalin and toluene (or ethylbenzene) at 20° differ by about a factor of 5, as compared with a factor of 12 for polyisobutylene solutions and a factor of several hundreds for polystyrene solutions in these solvents. Hence, viscosity differences between solutions of polymers depend on the viscosity of the solvent but are not wholly determined by it. The basic reason for differences in fluidity of solutions in different solvents is component interaction. Therefore it is very important to compare viscosities with parameters which characterise the interaction: as far as possible, the comparison should apply to the same concentration region.

† It may be useful to stress that when comparing any property of solutions in different solvents one should not use weight fractions, since their value depends on the density of the liquid. The concentration of the solution should be given in mole or volume fractions. Using the former units we compare the solutions at a constant concentration of solvent molecules, using the latter units we compare them at a constant degree of filling of space by different solvents. With a property such as viscosity it is more correct to compare solutions of equal volume fraction.

We must first of all consider the thermodynamic affinity between the polymer and the solvent, measured by the chemical potential difference $\Delta\mu_1$ or by the second virial coefficient A_2. Experimentally measured values of $\Delta\mu_1$ and A_2 show that iso-octane is a good solvent for polyisobutylene whereas butyl propionate is a poor solvent[81]. In the composition range between $\varphi_2 = 0.5$ and $\varphi_2 = 1$ the viscosity coefficients of polyisobutylene solutions in the two solvents are identical. Decalin is a poor solvent for polystyrene, whereas ethylbenzene is a good solvent. In the former the viscosity and the heat of activation are much higher than in the latter. But ethyl acetate also is a poor solvent for polystyrene, yet the viscosities of ethyl acetate and ethylbenzene solutions are very similar. Thus, there is no correlation between the viscosity coefficient of a solution and the thermodynamic affinity of the polymer for the solvent. Hence, it is not generally correct to assume, over a wide concentration range, that the viscosity or the heat of activation of a solution in a thermodynamically more active solvent must be higher (or lower) than in a poor solvent.

It must be noted that no correlation is observed between viscosity and the heat of dissolution (i.e. the enthalpy change). Knowing the differences in chemical potential of a component, $\Delta\bar{\mu}_i$, and its partial enthalpy, $\Delta\bar{H}_i$, we can calculate the partial entropy of mixing, $\Delta\bar{S}_i$:

$$\Delta\bar{\mu}_i = \Delta\bar{H}_i - T\Delta\bar{S}_i. \qquad (31)$$

The entropy of mixing is largely determined by the flexibility of the polymer chain[72,75]. When flexible polymers are dissolved the partial entropy of mixing of the solvent $\Delta\bar{S}_i$ is always greater than in the dissolution of polymers with rigid chains, since in the former case the number of configurations which the chains can adopt in solution (and therefore also the thermodynamic probability of the solution) is greater than in the latter.

For polyisobutylene solutions, the values of $\Delta\bar{S}_i$, which characterise the flexibility of the polymer chain, decrease along the following series of solvents: toluene > CCl_4 > > iso-octane ≃ cyclohexane[81].

Thus, in solutions of elastic polymers solvent interactions take the form of changes in the flexibility of the chain. The viscosity of the solution is lowest in the solvent which makes the polymer chain most flexible, as was to be expected from the general theoretical considerations outlined above. However, the viscosity of the solvent itself also plays a role, and on occasions these two factors can be mutually opposing. Thus, the viscosity of CCl_4 is greater than that of iso-octane by about a factor of two, but the polyisobutylene chain is less flexible in iso-octane solutions than in CCl_4. The two factors cancel each other out, and the two solutions have identical viscosities.

At elevated temperatures the rate [amplitude?] of the torsional vibrations of the units increases: the kinetic flexibility of the polymer chain increases, the whole set of conformations becomes available[82], and the influence of the nature of the solvent becomes less marked. At a certain temperature, solutions of equal φ_2 in solvents of equal viscosities have the same viscosity. This is very clearly seen for solutions of polyethylene at $T > T_f$: the viscosities of solutions in decalin, dodecane, xylene, and monochlorobenzene lie on a common curve[69].

Thus, we can make the following statement regarding the viscosity of polymer solutions at experimental temperatures higher than T_g: the lower the viscosity of the

solvent and the greater the flexibility of the polymer chain in that solvent, the lower will be the viscosity of the solution.

The situation is a great deal more complicated when T_g for the dissolved polymer is significantly higher than the experimental temperature: this is particularly true of polymers with polar side-chain substituents which interact strongly both with each other and with the solvent molecules. In this case it is impossible to explain the effect of solvent on the viscosity of concentrated polymer solutions without detailed consideration of the structure of solutions.

II. NEWTONIAN VISCOSITY AND STRUCTURE OF THE SOLUTIONS

Studies of the viscous, optical, and other properties of very dilute polymer solutions show that the individual macromolecules have a coiled, globular form, and can move independently of each other[80]. This model applies only to very dilute solutions; when the concentration is increased the molecules begin to interact. The problem, therefore, is to identify the concentration at which these interactions set in and the configuration of the interacting molecules.

As long ago as in 1931 Staudinger[83] proposed the idea of a "critical" concentration, i.e. a concentration at which rod-shaped polymer molecules begin to touch. Boyer and Spencer[84] prefer to redefine the "critical concentration" as the concentration at which a random distribution of globular molecules becomes close packed. Their calculations show that the critical concentration depends on the molecular weight of the polymer and on the nature of the solvent. Thus, for solutions of polystyrene in benzene C_{crit} (g/100 ml) = $= 30.6M^{-1/2}$, whilst for solutions of polystyrene in ethyl methyl ketone $C_{crit} = 69.1M^{-1/2}$. When the molecular weight is $\sim 10^6$, $C_{crit} = 0.03-0.06$ g/100 ml (i.e. is very small). Using modified Ostwald viscometers with very narrow capillaries (d = 0.2 mm and 1600–3900 s outflow time for the pure solvent), Streeter and Boyer[85] observed anomalies in the viscosity at high dilutions. Their results show that the corrected viscosity varies linearly with concentration only down to 0.1 g/100 ml: further dilution gives a sharp upward bend in the curve, and still further dilution (below C = 0.002 g/100 ml) makes the curve bend down again, forming a maximum. Critical concentration values of 0.03–0.07% were obtained from these experiments[85], but subsequent work failed to confirm the results. Thus, Frank[86] did not observe any anomalies in the concentration dependence of the light-scattering asymmetry of the same solutions. Öhrn suggested[87], as a result of his calculations, that the phenomena observed by Boyer and coworkers were due to adsorption of polymer molecules on the viscometer walls, resulting in a decrease in diameter as well as a decrease in concentration. By working with a viscometer provided with three capillaries of different diameters he found that the largest anomalies are observed with the narrowest capillaries. Batzer's studies[88] of the viscosity of poly(vinyl chloride) solutions with different degrees of chain branching support this explanation. Therefore we must conclude that the effects observed by Streeter and Boyer have no bearing on the existence of a critical concentration.

Interest in this problem has been renewed in recent years. Horth and Rinfret[89] studied the concentration dependence of the density of poly(vinyl acetate) solutions, and concluded that a "critical" concentration exists, varying from 0.75 to 0.09 g/100 ml as the molecular weight varies from 80 000 to 3 200 000. From their measurements of the concentration dependence of the heat of mixing of poly(vinyl acetate) with methanol and tetrachloroethane Parent and Rinfret[90] obtained appreciably lower values of the critical concentration (φ_2 = 0.02–0.005).

We feel that the term "critical" is an unfortunate one, because the properties of the solutions as a rule do not vary discontinuously with concentration. The so-called singular points on property–composition curves are due to the presence of specific interactions between the components[91]. Experimental observations of density discontinuities at a strictly defined concentration are also unconvincing: no discontinuities were observed in analogous measurements on polystyrene and polyisobutylene solutions[76]. What is undeniable, however, is that the macromolecules begin to interact at some definite level of concentration which must be a function of the molecular weight of the polymer and of the nature of the solvent: under these conditions the solutions contain aggregates or associations of molecules rather than individual molecules. Polymer association effects have been discussed even in dilute solutions[92–95]. The interaction forces will depend, of course, on the nature of the polymer and of the solvent: dipole–dipole interaction predominates in poly(vinyl chloride) solutions in polar solvents, whilst in solutions of polybutadienes in octane or chloroform dispersion interactions are predominant. The latter are quite substantial if allowance is made for the increase in polarisability with molecular length. But this interaction is invariably present, and associations are formed.

It remains to be established what these associations consist of, how the macromolecules are distributed within the associations, and what is the configuration of the macromolecules. Boyer and Spencer assumed, in their first paper, that the globular molecules remain unchanged in form when they come into contact, but they were subsequently forced to postulate unwinding or uncoiling during interaction. The view that uncoiling must take place when the macromolecules interact follows directly from our knowledge of the structure of the polymers themselves, which are often prepared by concentrating their solutions. With the exception of a few ("globular") polymers, the polymers themselves do not contain unchanged globular formations. According to the views current until very recently, an amorphous polymer consists of a conglomeration of entangled, more or less straight, molecular chains, whereas in a crystalline polymer ordered regions alternate with regions of entangled chains. The entangled chain model was adopted in the theory of the viscosity of concentrated solutions, whose basic postulate is that all the chains are mutually intertwined as in a ball of tangled threads. The number of interlocks increases with the molecular weight of the polymer.

However, as Kargin and coworkers were the first to point out[96], the concept of tangled chains does not apply to a real polymer. Very large numbers of so-called supermolecular structures have been reported in polymers, and it has been shown that even in the amorphous state polymers have an ordered bundle-like structure[97]. The formation of bundles of chains, observed in amorphous polymers, must be preceded by uncoiling and mutual orientation of the chains.

Since very dilute solutions contain globular molecules whereas in the polymers themselves the chains are rela-

tively straight, the first effect must be an unfolding or uncoiling of the globular molecule as the solution becomes more concentrated: this has been confirmed by an electron-microscopic study of poly-α-butylene solutions[98]. Colophony (a substance whose glass point is above room temperature) was used as the solvent, thus enabling the structure of the solution to be "frozen" during the investigation. It was found that in poly-α-butylene solutions of concentration 0.1–0.5%, the molecules have a linear configuration and interact with each other to give appreciably ordered formations. These experiments suggest that individual globular molecules are to be found only in the more dilute solutions.

Unfortunately, it is impossible at present to examine the structure of the more concentrated solutions in the electron microscope, and therefore the indirect methods of investigation such as light scattering and viscosity studies play an important role. The first indications of the uncoiling of chains in polyelectrolyte solutions with increase of concentration and of degree of ionisation came from viscosity studies[99]. Zubov and Lipatov explain the sharp increase in viscosity obtained by concentrating aqueous solutions of poly(methacrylic acid) by postulating uncoiling of molecular chains and the formation of supermolecular structures[100]. A similar unfolding of globular molecules occurs in solutions of polymeric non-electrolytes.

Recently, an attempt was made[101] to estimate the shape of interacting macromolecules by comparing the concentration dependence of the relative viscosity of polymer solutions with that of suspensions of rigid spherical particles. It was concluded that the ratio $\log\eta_{rel}/C$ (where η_{rel} is the relative viscosity) increases gradually with the former, but decreases with the latter, when the concentration increases. The author[101] ascribes this difference to different interaction mechanisms. The collision of two rigid spheres produces a "dumb-bell", which contributes to the viscosity more than each isolated sphere. On the other hand, when two polymeric molecules collide, molecular aggregates are formed, and these contribute less to the viscosity than the two separate macromolecules. The papers by Maron and coworkers[102,103] contain similar conclusions, from viscosity data, on the change in shape of interacting particles.

Thus, when the concentration of a polymer solution is increased the globular molecules unfold, and the chains, more or less straightened, begin to interact. This is accompanied by a sharp increase in light scattering by the solution, which decreases, however, when the concentration is increased still further[104].

In the concentration region where light scattering decreases, the viscosity rises steeply, evidently due to the formation of a continuous disordered network in the solution. However, this network is composed of aggregates of more or less linear chains rather than of interlocking and entangled long molecular chains. Interlocking of macromolecules in solutions is as unlikely as it is in polymers, because it would be inconsistent with the observed rapid establishment of equilibrium in solutions following temperature or concentration changes. The relaxation time of chains is very large, and unravelling processes should be exceedingly slow. In practice (in the neighbourhood of a phase separation temperature, say) a turbid solution becomes instantly transparent, corresponding to the appearance of a maximum on the viscosity polytherm[105,106]. This is evidence that the solution contains aggregates which can rapidly regroup in response to a temperature change.

When the concentration of the solution is increased the degree of aggregation also increases, the network becomes more ordered, and fluctuations in concentration decrease. This is accompanied by a continuous increase in viscosity and by a decrease in the intensity of excess light scattering.

The non-linearity of the changes in heat of activation for the viscous flow of polymer solutions and the sharp increase of ΔH_{visc} at $\varphi_2 > 0.5$ are evidence for the existence of a concentration region in which interactions between chains are very strong. In this region of compositions we are evidently dealing with the highly ordered supermolecular structures which are found in the polymers themselves.

Hirai has derived[107], on the basis of the concept of bundles or "beams" of chains in solutions, a theoretical equation for the dependence of the heat of activation for viscous flow upon concentration and molecular weight of the polymer: this equation corresponds exactly to the experimental curves shown in Fig. 10.

Thus, the whole of the available experimental data on the viscosity and light scattering properties of concentrated polymer solutions points to the existence, in polymer solutions, of a number of concentration regions with different degrees of order and chain conformations: (1) the region of dilute solutions, in which the globular molecules become uncoiled and form aggregates as φ_2 is increased; (2) the concentration region in which the aggregates combine into a continuous network whose degree of order increases with φ_2; (3) the region of very concentrated solutions, in which highly ordered supermolecular structures are formed. All the transitions are reversible both towards concentration and towards dilution.

Thus, when a polymer comes into contact with a low-molecular liquid the molecules of the latter penetrate only between the ordered supermolecular structures (interbundle swelling). This is true whether the liquid is a good solvent or a poor solvent. According to the size of the solvent molecules, and to their affinity for the polymer, disintegration of the bundles may occur in different ways; hence the size of the supermolecular structures at a given value of φ_2 depends on the nature of the solvent. In decalin solutions of polystyrene the bundles do not break down appreciably, whilst in ethylbenzene solutions substantial disintegration occurs: the viscosity of the former solutions at 25° is much greater than that of the latter. In the high concentration region the viscosity of polyisobutylene solutions is the same in a good solvent (iso-octane) as in a poor solvent (butyl propionate). This also suggests that the molecules of these liquids penetrate only between the bundles, whose existence has been proved for the case of rubber-like polymers[108]. Butyl propionate cannot penetrate into the bundles and the swelling is limited. Iso-octane can enter the bundles, so that the latter disintegrate and the degree of ordering decreases. At a definite concentration (which is lower the better the solvent) the molecules begin to break apart and only at very low concentrations can we expect isolated globular macromolecules to form.

All that has been said agrees satisfactorily with Kargin and Kozlov's recent views[109,110] on interbundle plasticising, and is in keeping with a general flow mechanism common to polymers and their solutions. According to generally accepted ideas, based on the fact that polymers and low-molecular liquids have very similar heats of activation for viscous flow, the elementary unit of flow of a polymer is a

chain segment. However, the heats of activation [fluidity?] of polymers and of their concentrated solutions are higher than those of liquids by one order of magnitude, and those of glassy polymers are higher by two orders of magnitude. This suggests that the jumps involve portions of a bundle rather than individual segments, i.e. that the viscous-flow properties are determined by the collective motion of chains[1].

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ADVANCES IN THE SYNTHESIS OF UNSUBSTITUTED AMINO-ACIDS

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Recently there has been a considerable increase of interest in the synthesis of biologically important amino--acids, due to the fact that these amino-acids are ceasing to be objects of theoretical studies only and are becoming available as products of industrial manufacture and are widely used in the food industry and in agriculture. Since the number of studies published recently in this field is fairly large, their critical review is essential.

The present review is concerned with the synthesis of eight unsubstituted amino-acids: valine, leucine, isoleucine, phenylalanine, threonine, lysine, methionine, and tryptophan. A review on the synthesis, degradation, and racemisation of yet another important amino-acid, glutamic acid, was published in 1963.[1] Since the detailed review of the literature on the synthesis of amino-acids in the book of Greenstein and Winitz[2] covers the original literature up to 1958, we shall consider in detail only later studies which appeared up to the middle of 1965 and also some work published in the second half of 1965. Earlier work will be quoted for the purpose of exposition. Initially we shall describe general methods of synthesis and then specific methods for each individual amino-acid, starting with monoaminomonocarboxylic acids and then continuing with more complex acids. Since the usual chemical syntheses yield racemic amino-acids, the separation of the DL-forms into optical isomers is of primary importance. Among the reviews dealing with this problem, there is one which was published relatively recently[3]. However, all these reviews describe only individual aspects of the problem and are to a large extent obsolete.

GENERAL METHODS OF SYNTHESIS

The simplest general method of the synthesis of all amino--acids is the ammonolysis of the corresponding α-halogeno--substituted acids. The amination reaction itself presents no difficulties and the applicability of this reaction is restricted solely by the availability of the α-halogeno-acids. Until recently the halogeno-derivatives of aliphatic acids only were available. In 1956–1959 Nesmeyanov, Freidlina, and coworkers developed a new method for the synthesis of α- and ω-chlorocarboxylic acids and their derivatives with other functional groups based on the telomerisation of ethylene[4,5]. $\alpha\alpha\alpha\omega$-Tetrachloroalkanes, obtained in the radical--chain telomerisation of ethylene and carbon tetrachloride, are converted into amino-acids according to the following general mechanism:

$$CCl_3CH_2(CH_2)_nCl \xrightarrow[SbCl_5]{FeCl_3,\ AlCl_3} CCl_2=CH(CH_2)_nCl \xrightarrow{HX} \rightarrow CCl_2=CH(CH_2)_nX \xrightarrow[CH_3COOH\ or\ (CH_3COO)_2Hg]{Cl_2/H_2SO_4} HOOCCHCl(CH_2)_nX \xrightarrow{NH_3} HOOCCH(NH_2)(CH_2)_nX,$$

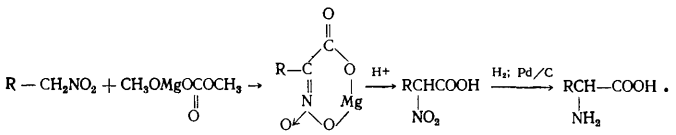
where X is the substituent and n ranges from 0 to 15.

The following amino-acids were obtained in this way: phenylalanine (X = C_6H_5, n = 1), glutamic acid (X = COOH, n = 2), and lysine and ornithine [X = $C_6H_4(CO)_2N$, n = 4 and 3]; the phthalic acid group was removed by hydrolysis with concentrated hydrochloric acid. Ammonolysis of $\alpha\omega$-dichlorovaleric acid (X = Cl, n = 3) yields proline[7-9].

α-Nitro-acids and their derivatives constitute another convenient intermediate for the synthesis of α-amino-acids. In 1952 Weisblatt and Little outlined the principal ways of using nitroacetic ester for the synthesis of α-amino-acids: (1) alkylation of nitroacetic ester with alkyl halides, alkylarenesulphonates, and alkyl sulphates in the presence of alkaline catalysts, with carbinols in the presence of boron trifluoride, and with substituted dialkylamines and quaternary ammonium bases; (2) condensation of nitroacetic ester by reaction of the Knoevenagel type with aldehydes

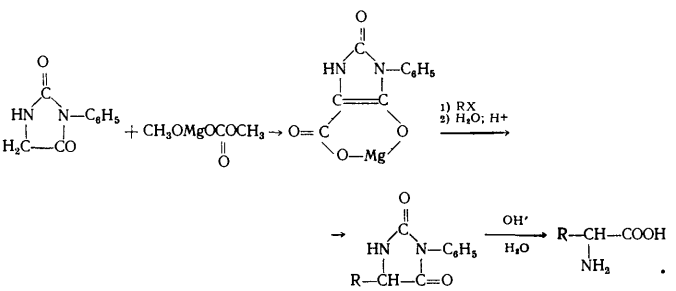
and ketones in the presence of the appropriate catalysts; (3) addition of nitroacetic ester to substances containing an activated double bond. After the introduction of the required substituents, the nitro-group is reduced and the ester is hydrolysed[10]. These workers and a number of other investigators developed, on the basis of nitroacetic ester, methods for the synthesis of tryptophan[11], threonine[12,13], leucine[14], glutamic acid[15], glycine[16,17], α-aminobutyric acid[13], and other amino-acids. Interest in nitroacetic ester has recently increased appreciably in connection with the development of a simple method for its preparation from nitromethane and alkali[18]. Nitromalonic ester has also been used for the preparation of tryptophan[19-21], proline[22], ornithine[23], and glutamic acid[24]. Valine[25,26], leucine[26], isoleucine[27], and the *O*-methyl ester of threonine[26] have been obtained by the reduction of the esters of substituted α-nitroacrylic acids. The α-nitro-ϵ-lactams of these acids[28] can apparently be used as intermediates in the synthesis of $\alpha\omega$-diamino-acids.

For the preparation of α-nitro-acids, Finkbeiner proposed a reaction involving the carboxylation of primary nitro-paraffins with methoxymagnesium methyl carbonate in dimethylformamide[29-32]:



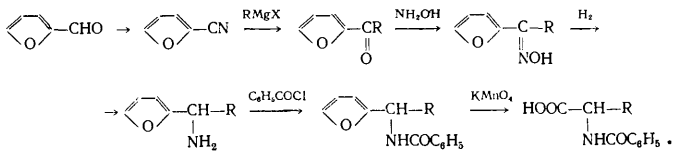
The chelate structure of the magnesium salt of the α-nitro-acid formed stabilises the molecule. The free nitro-acid is isolated by acidification and then reduced to the amino-acid. DL-Alanine, DL-α-aminobutyric acid, and DL-norvaline were obtained in this way from nitroethane, 1-nitropropane, and 1-nitrobutane in yields of 46, 34, and 42% respectively, relative to the nitro-paraffin; the authors state that the conditions used were not optimum[29].

The general synthesis of amino-acids by the carboxylation and alkylation of phenylhydantoin was achieved with the aid of methoxymagnesium methyl carbonate:



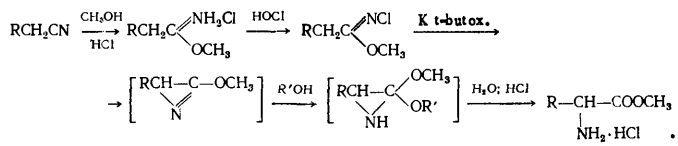
The following amino-acids were obtained by this procedure (the amino-acid and the alkylating agent are listed, the percentage yield with respect to 3-phenylhydantoin being indicated in brackets): valine, isopropyl bromide (38); leucine, isobutyl bromide (46); phenylalanine, benzyl chloride (97); tryptophan, gramine (53); proline, 1,3-dibromopropane (45); lysine *N*-(4-bromobutyl)phthalimide (45); glutamic acid, the sodium salt of β-chloropropionic acid (30).[33,34]

In 1958 Terent'ev and Gracheva suggested that furfural be used as a cheap raw material for the preparation of amino-acids[35]. Furfural is converted into a ketone which is in turn converted into the corresponding oxime, the latter being reduced to the amine with zinc in acetic acid. The amino-group is then protected by acylation, the furan ring is oxidised with alkaline permanganate, and the acyl derivative of the amino-acid is obtained, the free acid being isolated after hydrolysis:



The *N*-benzoyl derivatives of the following aliphatic amino-acids were obtained in this way: leucine, alanine, norvaline, norleucine, α-aminobutyric acid, and α-amino-isoheptanoic acid [R = $CH_2CH_2CH(CH_3)_2$]. When *N*-benzoyl-isopropylfurylamine is oxidised, the valine derivative cannot be isolated[36]. In addition, *N*-benzoylaspartic acid and proline were obtained from the furan derivatives[37]. β-Amino-acids are obtained by the condensation of furfural and nitro-alkanes with subsequent reduction of the nitro-group with lithium aluminium hydride and the oxidation of the furan ring[38]. The aldol condensation of furfural with alkyl methyl ketones, accompanied by the hydrogenation of the unsaturated ketone, ammonolysis, and oxidation, yields γ-amino-acids[39].

Baumgarten proposed a very interesting method for the conversion of nitriles into α-amino-acids. The reaction proceeds as follows:



Partial hydrolysis of the nitrile yields the hydrochloride of the methyl imino-ester, which is converted into the *N*-chloro-imino-ester by chlorination. The latter undergoes rearrangement into the methyl ester of the amino-acid hydrochloride under the action of potassium t-butoxide. The rearrangement is a special case of the conversion of *N*-dichloro-s-alkylamines into α-amino-ketones. The following amino-acids were obtained from nitriles (the percentage yields with respect to the nitrile are indicated in brackets): phenylalanine (44), leucine (59), alanine (51), glycine (51), norvaline (21), and phenylglycine (51).[40]

We think it desirable to consider in the general section the following widely known synthetic methods for amino-acids.

1. Syntheses based on malonic, acetamidomalonic, cyanoacetic, and acetoacetic esters.

2. The azlactone method for the synthesis of aromatic amino-acids and the related procedures which are based on the principle involving the utilisation of the mobility of the hydrogen atoms of the activated methylene group (condensation of aldehydes with dioxopiperazines, hydantoins, etc.).

3. The cyanohydrin method (the Strecker synthesis).

4. The applications of the Schmidt method in the synthesis of amino-acids.

The new variants and the most important examples of the application of these methods will be examined in fair

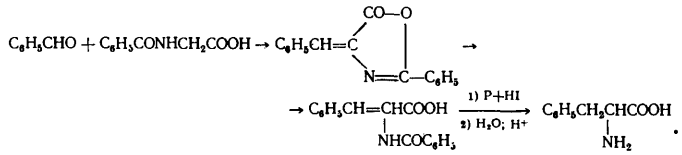
detail in connection with the description of the procedures for the preparation of the individual amino-acids.

The problems associated with the synthesis of mixtures of amino-acids from the simplest carbon and nitrogen compounds under the action of various physical factors (temperature, irradiation, ultrasonic vibrations, electric discharge, etc.) are outside the scope of this review.

Phenylalanine

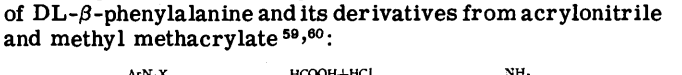
The principal methods for the synthesis of phenylalanine are at the same time the general methods for the preparation of other aromatic and aliphatic monoaminomonocarboxylic acids. Therefore in the subsequent consideration of the syntheses of valine, leucine, and isoleucine we shall refer to the reactions described in this section.

The method proposed by Erlenmeyer (known as the Erlenmeyer synthesis) for the synthesis of aromatic amino-acids by the condensation of benzaldehyde (or other aromatic aldehydes) with hippuric acid is widely known. The azlactone formed hydrolyses and after reduction and liberation of the amino-group phenylalanine is obtained[41]:



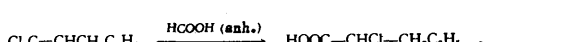
The yield of phenylalanine is 63–67% with respect to the azlactone[42] or 55% with respect to hippuric acid[43]. When acetylglycine is used instead of hippuric acid, the yields reach 72%.[44-46] Various modifications of this method are known, consisting in the condensation of benzaldehyde with heterocyclic compounds containing an active methylene group: hydantoin[47-50], dioxopiperazine[51], 1-benzoyl-2-mercaptohydantoin[52,53], 2-mercaptothiazolone[54,55], and rhodanine[56]. Reduction and hydrolysis of the resulting benzylidene derivatives yields amino-acids.

The application of the Meerwein reaction proved extremely fruitful in the synthesis of aromatic amino-acids, in particular phenylalanine and tyrosine[57-61]. A very convenient method for the preparation of α-halogeno-β-arylpropionic and β-arylisobutyric acids, based on the halogenoarylation of acrylic acid derivatives, was developed, which made it possible to find a general method for the synthesis of DL-β-phenylalanine and its derivatives from acrylonitrile and methyl methacrylate[59,60]:



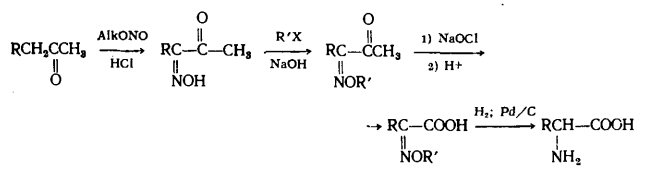
where X = Cl or Br.

α-Chloro-β-phenylpropionic acid was obtained in 40% yield; when it was aminated with aqueous ammonia, the yield of phenylalanine was 40–42%, the use of liquid ammonia increasing the yield of the amino-acid to 80%. The halogenoarylation of acrylic acid with subsequent amination gave phenylalanine with an overall yield of 10% with respect to aniline[61]. Another method for the preparation of α-chloro-β-phenylpropionic acid was proposed by Freidlina and coworkers:



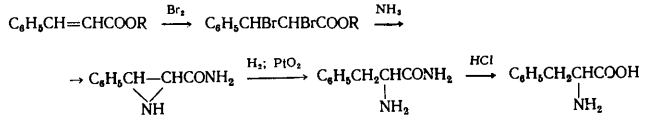
The acid, isolated in 63% yield, was subjected to ammonolysis with an excess of aqueous ammonia under pressure, the product being phenylalanine in 77% yield[7].

Monoaminomonocarboxylic acids can be obtained from alkyl ethyl ketones via α-hydroxyimino-ketones by the following mechanism:

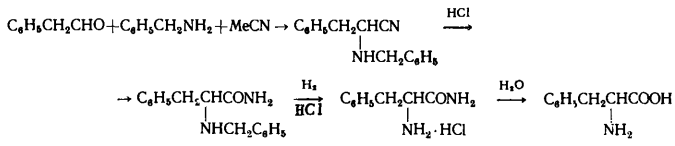


The methyl ketone is nitrosated with alkyl nitrite or an alkali metal nitrite, the ketone oxime being alkylated with diethyl sulphate. Hoffmann degradation of the α-alkoxyimino-ketone gives the α-alkoxyimino-acid, which is reduced to the amino-acid. In this way it was possible to obtain phenylalanine from methyl β-phenylethyl ketone in 50–53% yield, alanine from ethyl methyl ketone in 14 and 32% yield, and valine from isobutyl methyl ketone in yields of 34 and 31%.[62-65] In addition, tyrosine, norleucine, 3,4-dihydroxyphenylalanine, and phenylglycine were also obtained[66].

Interesting reactions occur in the preparation of phenylalanine from cinnamic esters. The cinnamic acid ester is converted into the ester of αβ-dibromo-β-phenylpropionic acid by treatment with bromine. The product obtained when this ester is treated with an excess of 25% solution of ammonia under pressure was initially incorrectly assumed to be the amide of α-amino-β-phenylacrylic acid [$C_6H_5CH{=}CC(NH_2)CONH_2$].[67] Later it was shown that the compound is in fact a derivative of aziridine[68]. Hydrogenation of the intermediate product with subsequent hydrolysis gives phenylalanine in 25% yield with respect to the ester of αβ-dibromo-β-phenylpropionic acid[69]:



The synthesis of phenylalanine by the Strecker method was achieved by Erlenmeyer[70] in 1882 but has not been used since. In 1963 a modification of the method was proposed for the preparation of alanine, valine, leucine, and phenylalanine, consisting in the initial reaction of the aldehyde, metal cyanide, and benzylamine (instead of ammonia); the resulting (*N*-benzyl)amino-nitrile is hydrolysed to the amine, the benzyl group is removed by hydrogenation, and the amino-acid is obtained after hydrolysis[71]:



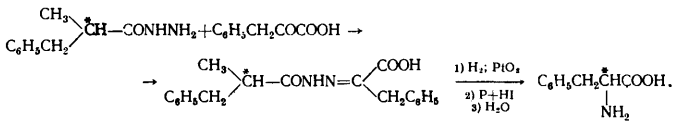
The methods for the preparation of phenylalanine with the aid of malonic, cyanoacetic, and acetoacetic esters and their derivatives are distinguished by their great variety. New modifications of these methods are being proposed by investigators also at the present time. Since a complete description of these syntheses would be unduly cumbersome and their exclusion from the review would render the range

of syntheses of unsubstituted amino-acids incomplete, we have confined ourselves to a Table in which the key features of the syntheses are given and other amino-acids obtainable by the same method are indicated.

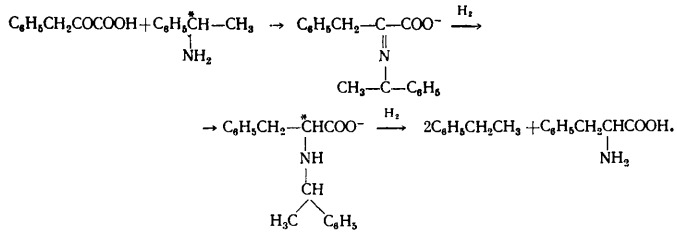
Reductive amination of phenylpyruvic acid with hydrogen and ammonia in the presence of the palladium catalyst is a reaction analogous to the reduction of oximes and phenylhydrazones of α-keto-acids[93]. Reductive amination is particularly convenient for the synthesis of phenylalanine labelled at the nitrogen[94]. A series of Japanese patents describe the reductive amination of phenylpyruvic, pyruvic, and oxoglutaric acids in the presence of various complex cobalt salts[95-97] and also with sodium borohydride[98]. The cobalt complexes were used in the preparation of phenylalanine by the hydrogenation of α-acetamidocinnamic acid[99].

The preparation of phenylalanine, leucine, and α-aminobutyric acid by the Grignard reaction has been noted. However, the yields of the amino-acids did not exceed 5–10%.[100]

Several methods have been proposed for the preparation of optically active phenylalanine (and also valine, alanine, and glutamic acid) by the reaction of substances containing an optically active group in the molecule, with formation of a new centre of asymmetry. However, the asymmetric yield is usually low. For example, the product of the condensation of the hydrazide of an optically active acid with an α-keto-acid is reduced and then decomposed, a compound with a new centre of asymmetry being obtained[101]:



The optical isomers of phenylalanine, alanine, and valine were obtained by the catalytic hydrogenation of the corresponding α-keto-acids in the presence of D(+)- and L(-)-α-methylbenzylamine:



The asymmetric centre of the amino-acid arises in the stage involving the hydrogenation of the Schiff base. The degree of asymmetry thus introduced depends on the structure of the initial substances and the properties of the catalyst[102]. The preparation of L-phenylalanine by the hydrogenation of α-acetamidocinnamic acid in the presence of Pd/C and small amounts of L-methionine[103] has been described. Akabori suggested that optically active amines and amino-acids be obtained with the aid of an asymmetric hydrogenation catalyst, consisting of a reduced protein–palladium complex prepared by the adsorption of $PdCl_2$ on fibres of silk fibroin. L-phenylalanine was obtained in this way from the ethyl ester of α-acetoxyiminophenylpropionic acid[104].

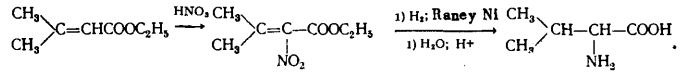
TABLE.

Starting material	No. of stages	Total yield, %	Other amino-acids obtained by the same method	Refs.
$C_6H_5CH_2CH(COOK)COOC_2H_5$	4	—		72
$CH_2(COOC_2H_5)_2$	4	31—36		73,74
$BrCH(COOC_2H_5)_2$	3	64		75
$C_6H_5CH_2CH(COOC_2H_5)_2$	2	60		76
$RCONHCH(COOC_2H_5)_2$	2			
$R=C_6H_5$		64		77
$R=CH_3$		60	histidine, leucine	78
$R=H$		60	aspartic and glutamic acids	79
$R=H$		75	norleucine, aspartic acid, and tyrosine	80
$RCONHCH(CONH_2)_2$ $R=C_6H_5$; CH_3	3	73—77	leucine, histidine, glutamic acid, and norleucine	81
$CNCH(NHCOCH_3)CONH_2$	3	77	valine, leucine, glutamic acid, and norleucine	82
$CN-CH(NHCOCH_3)-COOC_2H_5$	2	62	tryptophan, histidine, methionine, valine, and leucine	83
$CN-CH(CH_2C_6H_5)-COOC_2H_5$	2	30		76
$CN-CH_2COOC_2H_5$	5	18	valine and tyrosine	84
$CN-CH(NHCOCH_2C_6H_5)-COOCH_3$	2		leucine, methionine, and valine	85
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	3	54	alanine and aspartic and glutamic acids	86
То же	2	79		87
То же	2	68	alanine, leucine, isoleucine, methionine, valine, and tyrosine	88—92

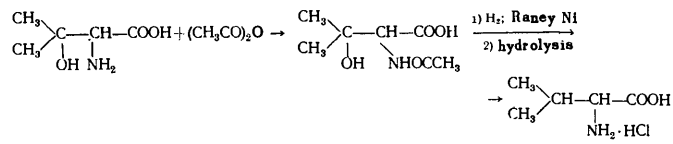
Valine

Valine is obtained most simply by the ammonolysis of α-halogenoisovaleric acid. When ammonia is allowed to act on α-bromoisovaleric acid, the yields of valine reach 78%;[105] treatment of the acid with hexamethylenetetramine results in almost quantitative yields of valine[74,106].

Various modifications of the Strecker synthesis have been examined by Gaudry[107]. Valine is obtained from isopropylmalonic ester in about 70% yield by the Schmidt reaction in a single stage[108]. The hydrogenation of the ethyl ester of ββ-dimethyl-α-nitroacrylic acid with subsequent hydrolysis results in the formation of valine in a yield of about 50%:[25,26]



The application of the Akabori method (see below) to the synthesis of valine merits attention. The *N*-acetyl derivative of hydroxyvaline obtained by the condensation of acetone with copper glycinate is reduced in the presence of Raney nickel, valine being obtained in 80% yield[109]:



A number of studies described in the preceding sections are also relevant to the synthesis of valine[33,62-65,82-85,88]. The failure in the attempt to obtain valine (and isoleucine) from furan derivatives[36] and also by the alkylation of the amides of acylaminomalonic acids[81] is probably due to steric hindrance.

Leucine

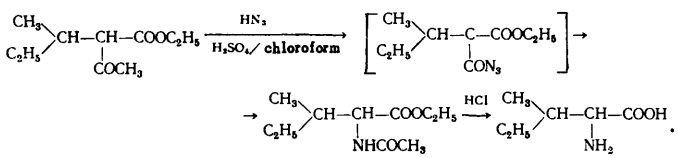
All the classical methods for the synthesis of amino-acids have been used in the preparation of leucine: amination of α-halogeno-derivatives of isocaproic acid with ammonia or hexamethylenetetramine, the Strecker synthesis from isovaleric aldehyde, and the syntheses with the aid of acetoacetic and malonic ester derivatives. Recently a number of new modifications have been proposed for the preparation of leucine [10,14,26,33,36,71,78,81-83,85,88,100,108].

Isoleucine

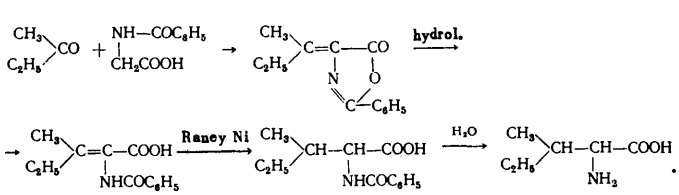
The difficulties in the synthesis of isoleucine are caused in the first place by the presence in this compound of two asymmetric carbon atoms, and hence of diastereoisomeric forms, and in the second place by the steric hindrance due to the large size of the s-butyl group. So far no methods are available for directed synthesis whereby isoleucine free from alloisoleucine could be obtained. The most favourable isoleucine : alloisoleucine ratio obtainable during synthesis is 3 : 1.

A 49% yield (after recrystallisation) of a mixture of racemic diastereoisomers containing 89% of DL-isoleucine was obtained by the bromination and amination of s-butylmalonic ester [110]. The use of acetamidocyanoacetic ester gives a 40% yield of the product with an isoleucine : alloisoleucine ratio of 3 : 1. [111] The mixture of diastereoisomers, obtained in a yield of about 60% in the reduction of the oxime of the ethyl ester of ethylmethylpyruvic acid [112] and also of its phenylhydrazone [88], contains up to 66% of isoleucine.

When isoleucine is synthesised by the Schmidt reaction, one obtains from s-butylacetoacetic ester a 40–50% yield of a mixture of racemic diastereoisomers, from which 72% of DL-isoleucine can be isolated [113,114]:



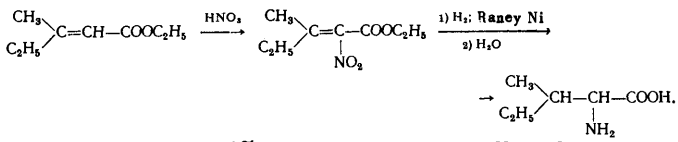
When s-butylmalonic acid is used in the same reaction as the starting material, the yield of the racemic mixture is 66%. [108] Certain modifications of the cyanohydrin synthesis make it possible to obtain a mixture of racemates containing more than 60% of isoleucine [115-117]. Attempts have been made to find stereospecific methods for the synthesis of isoleucine. 4-s-Butylidene-2-phenyloxazol-5-one, formed when ethyl methyl ketone was allowed to act on hippuric acid, was separated into two isomers by hydrolysis with alcoholic alkali. However, the subsequent reduction and hydrolysis of the *N*-benzoyl derivative of s-butylideneglycine involve partial inversion of configuration, and therefore the product contains only 78% of DL-isoleucine [113,118]:



In the preparation of isoleucine from the optically active D-isopentyl alcohol (by its oxidation to the aldehyde followed by synthesis using the cyanohydrin method) one obtains approximately equal amounts of L-isoleucine and D-alloisoleucine, which can be separated by crystallisation [119-121].

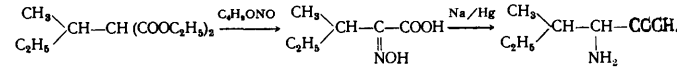
Two methods have been proposed for the conversion of s-butylcyanoacetic ester into isoleucine. The first is the Darapskii method (a modification of the Curtius rearrangement). In this case the ethoxycarbonyl group is converted into the amino-group ($COOC_2H_5 \rightarrow CONHNH_2 \rightarrow CON_3 \rightarrow \rightarrow NHCOOC_2H_5 \rightarrow NH_2$) and the carboxyl is obtained by the hydrolysis of the cyano-group. The second method is Hoffmann degradation ($CN \rightarrow CONH_2 \rightarrow NH_2$), which consists in the conversion of the cyano-group into the amino-group. The initial s-butylcyanoacetic ester has two asymmetric carbon atoms and is a mixture of racemic diastereoisomers, one of which predominates. Thus, the ratio of diastereoisomers in the resulting isoleucine depends on the method by which s-butylcyanoacetic ester is converted into isoleucine. (The investigators concerned suggest that there is no inversion of configuration in the amination and hydrolysis.) Indeed, when a non-purified ester obtained by the hydrogenation of the ethyl ester of α-cyano-β-ethyl-β-methylacrylic acid made from ethyl methyl ketone and cyanoacetic acid is used, the first method yields 60% of isoleucine in the mixture with an overall yield of the racemic diastereoisomers of 55%, while the second method gives 40% of isoleucine with an overall yield of 50%. [122,123] However, if the initial ester is made by the alkylation of cyanoacetic ester with s-butyl bromide, Darapskii's method gives 42% of isoleucine (overall yield 32%) [124] and the Hoffmann method gives about 60%. Consequently the ratio of the diastereoisomers in the initial s-butylcyanoacetic ester is not the same in the different methods of its preparation.

The amide of s-butylcyanoacetic acid is converted into isoleucine by the Hoffmann method in a single stage with a yield of 46%. [125] The yield of isoleucine obtained from the amide of s-butylmalonic acid is 74%. [126] s-Butylideneacetic acid prepared from ethyl methyl ketone and bromoacetic acid by the Reformatskii reaction can be converted into isoleucine in two ways. The first involves the usual operations: hydrogenation, bromination in the α-position, and ammonolysis. Isoleucine is then obtained in 32% yield, the isoleucine : alloisoleucine ratio being 71 : 29. The second procedure involves nitration with 81% nitric acid free from nitrogen oxides, followed by reduction:

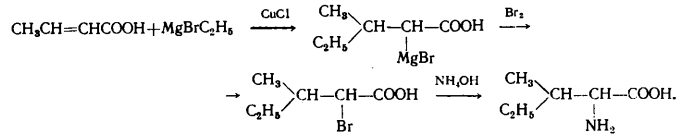


The yield is about 20% and the isoleucine : alloisoleucine ratio is 77 : 23.

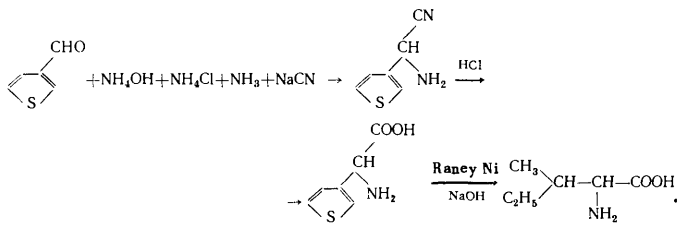
Isoleucine is formed in the reduction of α-hydroxyimino-β-methylvaleric acid obtained by the nitrosation of s-butylmalonic ester with butyl nitrite [114]:



A synthesis of isoleucine from crotonic acid using a Grignard reagent has been proposed recently [127]. It involves the following mechanism:



An interesting study has been made of the preparation of isoleucine from thiophen. 3-Thienylglycine obtained from thiophen-3-aldehyde by the Strecker method is subjected to reductive desulphurisation with Raney nickel, an equimolar mixture of DL-isoleucine and DL-alloisoleucine being obtained with an overall yield of 23%:

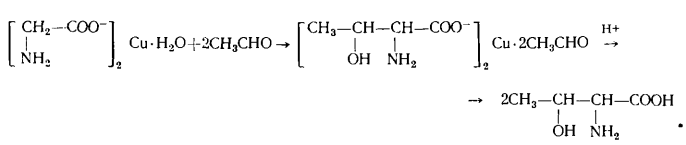


The 3-thienylglycine was separated into the optical isomers. Desulphurisation of the L-isomer gives a 21.5% yield of a product containing more than 50% of L-alloisoleucine. The investigators suggest that the conformation of the molecule adsorbed on the catalyst is stereochemically more favourable for the formation of the *allo*-form [128]. We shall see below, in the examination of the methods of synthesis of threonine, that those involving catalytic hydrogenation result in the preferential formation of the *allo*-isomer.

Threonine

The characteristic features of the chemical synthesis of threonine (α-amino-β-hydroxybutyric acid) are due to the necessity to introduce into the molecule both the amino- and the hydroxy-group. In the threonine molecule there are two centres of asymmetry (as in isoleucine) and therefore there exist two diastereoisomeric forms, of which only the L-*threo*-form is the natural amino-acid.

At the present time one may regard as the best the method of synthesis of threonine proposed by Akabori, which consists in the Knoevenagel condensation of the copper complex of glycine with acetaldehyde in the presence of alkaline reagents [129]:



In this reaction the complexed copper successfully combines the functions of activating the hydrogen atom in the methylene group and of protection of the amino-group. Since the copper complex of allothreonine is much more soluble than the threonine complex, the mixture of copper threoninates obtained in the reaction is convenient for the separation of the diastereoisomers [130-133]. The free amino-acids are isolated by the decomposition of the complex with hydrogen sulphide or on an ion-exchange resin. The amount of DL-threonine in the reaction product exceeds by a factor of two the amount of DL-allothreonine. This is virtually the principal value of the Akabori method, since other methods serve essentially for the preparation of allothreonine and the inversion of allothreonine into *threo*-threonine with thionyl chloride gives rise to additional difficulties and is not adequately effective [134,135].

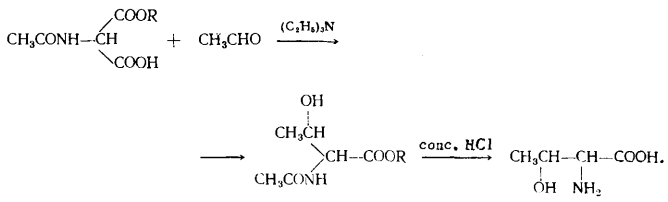
The undoubted advantages of the method described above include the small number of stages (two stages, including the isolation of the free amino-acid), good yields, speed, availability of the starting materials, and the possibility of regenerating the copper. A large number of papers and patents are devoted to the development of this method of preparing threonine. The principal results of these investigations are as follows. (1) The use of methanol as the solvent instead of water improves the yields and favours the formation of a purer crystalline product; (2) when the reaction is carried out under more severe conditions (elevated temperature, higher alkalinity of the medium), and the content of the *threo*-form in the product increases, but the overall yield falls (it has been shown that the copper complex of threonine is more stable under severe conditions than the complex of the *allo*-form); (3) the addition of pyridine increases the overall yield [129,136-143].

There is a patent describing the preparation of threonine (*threo* : *allo* = 3 : 1) by the reaction of copper glycinate with vinyl acetate in an aqueous medium in the presence of potassium carbonate [144].

Akabori investigated the reaction of acetaldehyde with cobalt triglycinate, which exists in two isomeric forms (α and β). The overall yield of the isomeric threonines, particularly with the β-form of the complex, is poorer than with copper glycinate, but the ratio of the *threo*- and *allo*--forms is more favourable (7.6 instead of 2.9). The poorer yield may be due to the much greater stability of cobalt glycinate compared with copper glycinate, and the change in the ratio of the *threo*- and *allo*-forms with temperature and duration of the reaction confirms that the stability of the cobalt threoninates is different [145]. An attempt has been made to obtain optically active threonine with the aid of the optically active cobalt complex of the type L-$[Co(EH)_2GLY]I_2$, where EH is ethylene- or propylene--diamine. The asymmetric yield of threonine was only about 8%. [146-148]

The possibilities of the Akabori methods are not restricted to the preparation of threonine. The use in this reaction of formaldehyde and other aldehydes and ketones and also of copper alaninate (instead of the glycinate) makes it possible to obtain a wide variety of α-amino-β-hydroxy--acids [109,149-154].

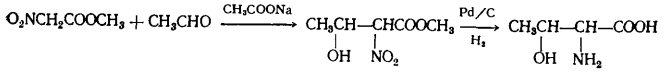
Recently a relatively simple general method has been proposed for the synthesis of α-amino-β-hydroxy-acids by the condensation of aldehydes with acetamidomalonic acid or its half-ester, which is a modification of King's method [155] (preparation of serine by the condensation of formaldehyde with ethyl acetamidomalonate):



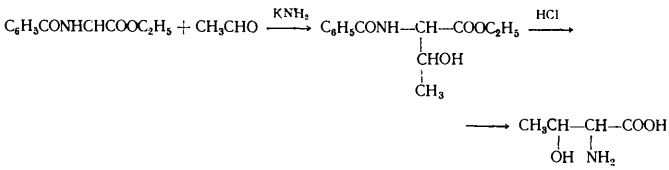
When R = H, serine is obtained in 50.4% yield and when R = CH_3, 53% of threonine consisting of 95% of the *allo*--form and 5% of the *threo*-form is obtained [156,157].

The synthesis of threonine based on nitroacetic ester is fairly simple and convenient. Methyl nitroacetate condenses smoothly with acetaldehyde, methyl α-nitro-β--hydroxybutyrate being obtained Its hydrogenation over

5% palladium on charcoal in a methanol–acetic acid mixture gives an equimolar mixture of the diastereoisomeric threonines with an overall yield of 66%:

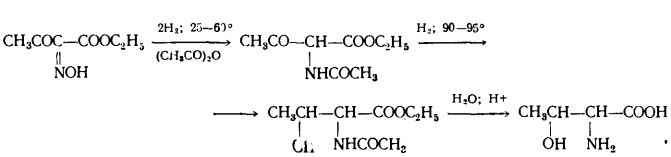


The reduction of α-nitrocrotonic acid in the presence of Raney nickel in methanol results, together with the normal reduction to α-aminobutyric acid, in the addition of methanol to the double bond and subsequent reduction to *O*-methylthreonine [13]. There are a number of patents describing syntheses of threonine. A 52% yield of threonine (the ratio of the *threo*- and *allo*-forms is not indicated) was obtained by the condensation of ethyl hippurate with acetaldehyde in the presence of alkali metal amides [158]:

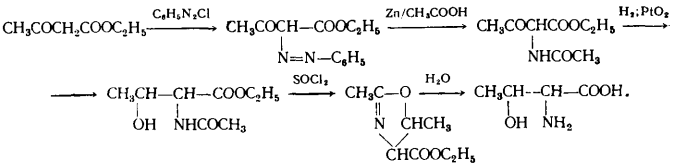


In another synthesis glycine and paraldehyde are condensed in dilute alcoholic solution of hydrochloric acid [159]. The treatment of the Schiff base obtained from aminoacetonitrile and formaldehyde with acetaldehyde followed by hydrolysis probably also yields threonine [160].

The syntheses of threonine from acetoacetic ester derivatives with a nitrogen-containing group in the α-position (=NOH or $=NOC_2H_5$; [161-163] $NHCOCH_3$; [170] $-N=NC_6H_5$ or $-NH-N(C_6H_5)(COCH_3)$ [164-169]) are based on the catalytic hydrogenation of the nitrogen-containing group to the amino-group and of the carbonyl group to the hydroxy-group. The reduction is performed in one or two stages (the nitrogen-containing group is reduced first and then the carbonyl group). The reaction involves 3–4 stages, but the amount of the *threo*-form in the mixture of epimers, which is obtained as a rule in a high yield, does not exceed 30–40% in the most favourable cases, the usual percentage being not more than 15–20. For example, threonine is obtained in an overall yield of about 70% from α-hydroxyiminoacetoacetic ester, the ratio of the *threo*- and *allo*-forms being 21 : 79: [162]

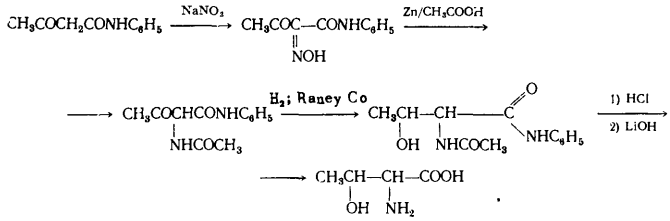


The preparation of threonine via the α-phenylazoacetoacetic ester has been investigated in detail:



After hydrogenation the product contains 80–85% of the *allo*-form of the ethyl ester of *N*-acetylthreonine. Under the action of thionyl chloride the configuration is inverted and a mixture containing 83% of DL-threonine is produced. The overall yield is 57%. [164]

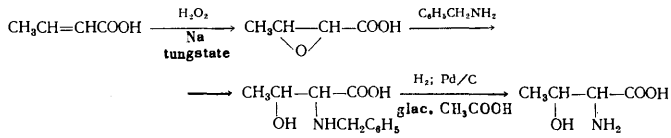
The use of a stereospecific hydrogenation catalyst, Raney cobalt, to increase the content of the *threo*-form in the mixture of diastereoisomers obtained by the reaction



has been described. The reaction products contain 56% of *threo*-threonine [171].

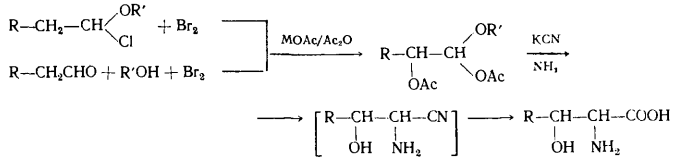
The first practical method of preparing threonine, which is also a general method for the preparation of α-amino-β-hydroxy-acids, was developed by Carter [172,173]. Its principle consists in the addition of hypobromous acid to unsaturated acids. It was established that this reaction takes place in only one way, with formation of α-bromo-β-hydroxybutyric acid (the second isomer, α-hydroxy-β-bromobutyric acid, does not form), which can be converted by amination into threonine, consisting mainly of the *allo*-form. Carter was the first to demonstrate the existence of threonine diastereoisomers, separated the epimeric racemates, isolated natural threonine, and investigated the interconversions of the *threo*- and *allo*-forms via the azlactone [174]. Modifications of this method are used for the synthesis of allothreonine [175-177].

The possibility of the selective synthesis of diastereoisomeric α-amino-β-hydroxy-acids has been demonstrated recently. Pure allothreonine was obtained in an overall yield of 50% by the following reaction [178]:



The epoxy-ring is opened in this process exclusively with the formation of the α-amino-β-hydroxy-acid, without admixtures of the α-hydroxy-β-amino-acid. Furthermore, ring opening takes place in such a way that the initial *trans*-form of the acid gives only *erythro*-isomers and the *cis*-form gives only *threo*-isomers. Unfortunately, the preparation of *threo*-threonine by this procedure has not been described; however, pure *threo*- and *erythro*-isomers of β-hydroxy-DL-aspartic acid have been obtained from maleic and fumaric acids [179].

Until recently Strecker's method for the synthesis of α-amino-β-hydroxy-acids has not been used, except for serine, since under the conditions of this reaction higher hydroxy-aldehydes isomerise to hydroxy-ketones. However, when acylal ethers of α-hydroxy-aldehydes are used, the reaction is successful:



M = Na for R containing up to three carbon atoms and M = Ag for R containing more than three carbon atoms. The yields

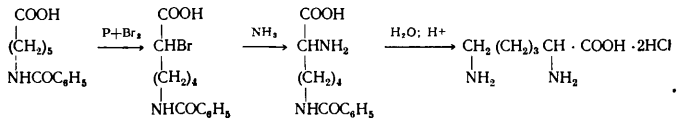
are 60–80% for R ranging from CH_3 to C_4H_9 and 45–60% for R ranging from C_5H_{11} to $C_{10}H_{21}$, i.e. are in general higher than is usual in the Strecker synthesis [180,181]. α-Alkoxypropionaldehyde is converted into threonine in 44% yield with the ratio *threo* : *allo* = 3 : 2. [182]

At the present time there are a number of fairly reliable methods for the quantitative and semi-quantitative estimation of the diastereoisomeric threonines in a mixture. These methods include paper chromatography [146], infrared spectroscopy [183], and gas–liquid chromatography [184,185].

Lysine

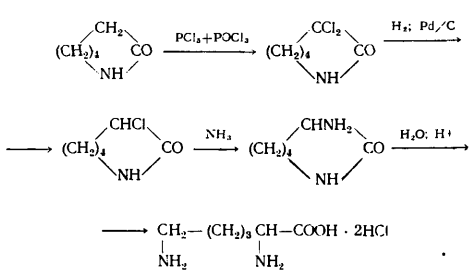
The problem of the chemical synthesis of lysine (αω-diaminocaproic acid) continues to attract the attention of many investigators. Among the methods available at present for the synthesis of lysine there are some which have been developed in detail and others which only provide a guideline for further research. To facilitate the exposition, the data have been grouped as follows: (1) syntheses of lysine from ε-aminocaproic acid derivatives, in particular from caprolactam; (2) syntheses based on telomerisation products; (3) syntheses by the cyanohydrin method; (4) other methods.

ε-Benzoylaminocaproic acid and caprolactam are the traditional starting materials for the synthesis of lysine. The at first sight simple problem, the introduction of only one amino-group into the α-position of an otherwise "finished" molecule, has been solved over a period of almost sixty years. In one of the first syntheses of lysine ε-benzoylaminocaproic acid was obtained in a three-stage synthesis from *N*-benzoylpiperidine and then converted into lysine as follows:

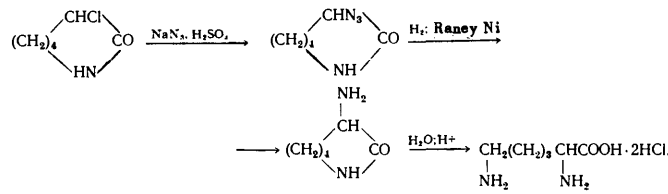


Although this synthesis is still extremely imperfect, it served as the basis for further studies [186]. Initially, caprolactam served as the starting material for the preparation of ε-benzoylaminocaproic acid. In many of the subsequent investigations improved methods of halogenation [187,188] and ammonolysis were employed (in particular bromination was replaced by chlorination with sulphuryl chloride) [189]. Rational utilisation of these advances made it possible to increase the yield of lysine from 23 to 68% with respect to caprolactam [190].

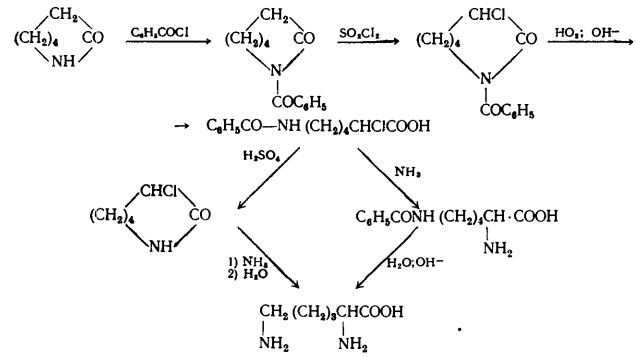
Later the attention of investigators was attracted to the possibility of direct halogenation and amination of caprolactam. It was found that in this case a complication arises in the halogenation, since two halogen atoms are introduced simultaneously into the caprolactam molecule, and in order to obtain α-chloro-ε-caprolactam it is necessary to reduce the dihalogeno-derivative formed initially:



A fundamental study has been made of the conditions of the chlorination and bromination of both caprolactam itself and its acetyl derivative, the conditions of the ammonolysis of α-halogeno-ε-caprolactam with aqueous and liquid ammonia in the presence of various salts, and the conditions of the hydrolysis of α-amino-ε-caprolactam. When optimum conditions are provided, the yield of lysine amounts to about 50% with respect to ε-caprolactam [191–193]. α-Amino-ε-caprolactam and then lysine can be obtained with the same yield by the reduction and subsequent hydrolysis of α-azido-ε-caprolactam [194,195]:

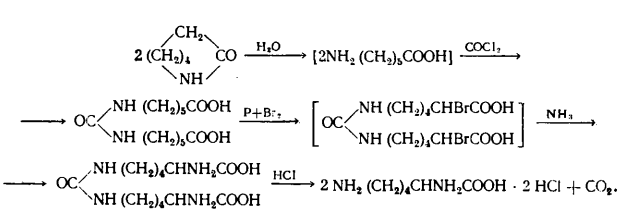


In contrast to ε-caprolactam, *N*-benzoyl-ε-caprolactam can be monochlorinated in the α-position. Then one obtains by alkaline hydrolysis ε-benzamido-α-chlorocaproic acid, whose subsequent conversion into lysine can be achieved in two ways:



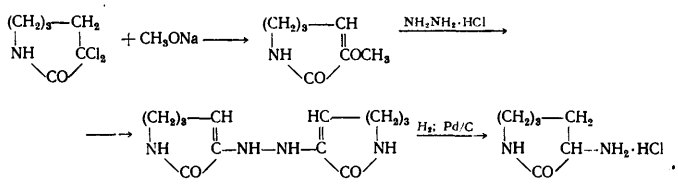
Amination with subsequent hydrolysis gives lysine in an overall yield of 73% and debenzoylation followed by hydrolysis and amination gives a 60% yield of lysine [196].

Apart from these procedures developed in detail, a number of modifications have been outlined, whereby it is possible to avoid certain difficulties in the existing syntheses, but these procedures require further development. For example, a new method has been proposed for the protection of the amino-group in aminocaproic acid with the aid of phosgene:

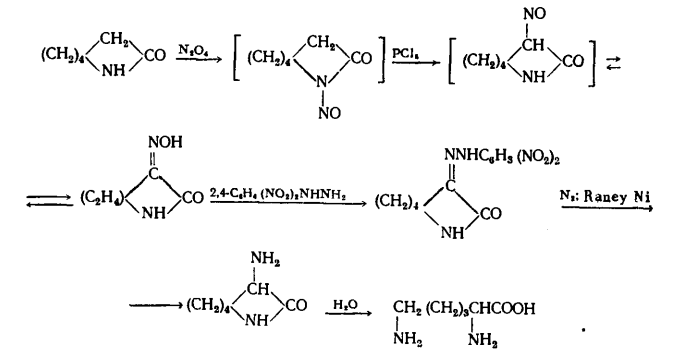


The overall yield of lysine is only 11%. [197,198]

A patent describes a method for the preparation of α-amino-ε-caprolactam from αα-dichloro-ε-caprolactam and hydrazine hydrochloride by the following mechanism[199]:

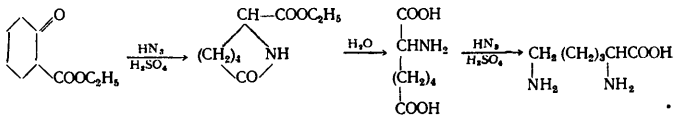


It has been shown that lysine can be synthesised via α-hydroxyiminocaprolactam. Treatment of caprolactam with nitrogen tetroxide gives an *N*-nitroso-compound, which rearranges into α-hydroxyimino-ε-caprolactam under the action of phosphorus pentachloride. The product is converted into the dinitrophenylhydrazone of α-oxo-ε-caprolactam from which α-amino-ε-caprolactam is obtained after hydrogenation:



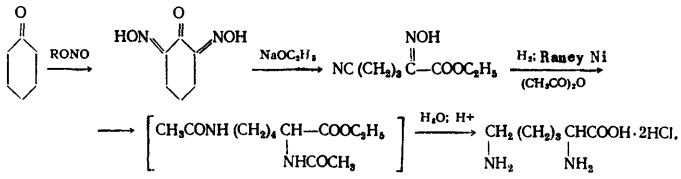
This fundamentally new reaction makes it possible to eliminate the halogenation stage[200,201].

The Schmidt reaction has been used in an interesting way for the preparation of lysine from 2-ethoxycarbonylcyclohexanone:



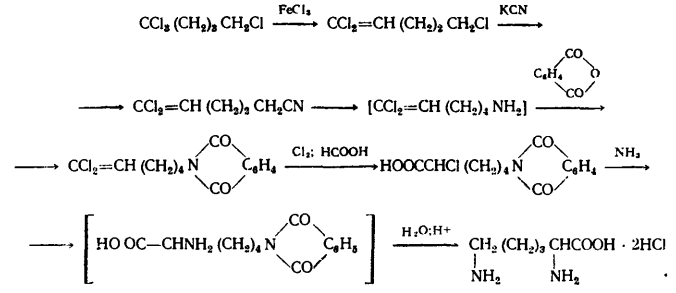
The overall yield is 60%. Only the ω-carboxy-group reacts[202].

It has recently been stated that α-nitro-ε-caprolactam can be used as the starting material for the synthesis of lysine[28]. An original procedure involving the use of cyclohexanone in the synthesis of lysine, which has been developed by Ferris, includes three stages: (1) preparation of 2,6-dihydroxyiminocyclohexanone by the nitrosation of cyclohexanone with alkyl nitrites in ether containing hydrochloric acid; (2) reaction of 2,6-dihydroxyiminocyclohexanone with sodium ethoxide in alcohol in the presence of acetic anhydride (Beckmann rearrangement of the "second kind")[203,204] with formation of the ethyl ester of 5-cyano-2-hydroxyiminovaleric acid; (3) hydrogenation of this ester in the presence of Raney nickel in acetic anhydride containing sodium acetate with subsequent hydrolysis using hydrochloric acid. The overall yield of lysine monohydrochloride is 63%:[205-208]

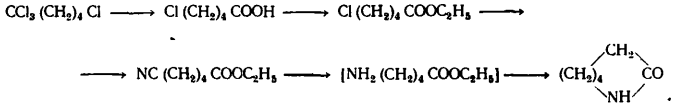


In a similar way ornithine was obtained from cyclopentanone and 4-methyl-lysine from 4-methylcyclohexanone[209,210].

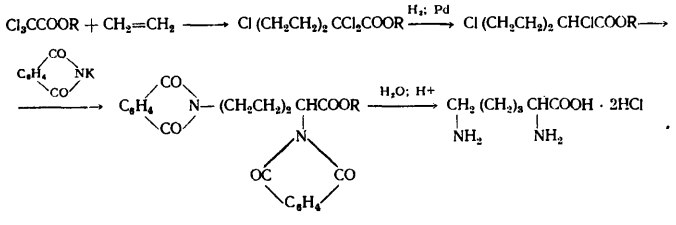
New possibilities arose in the field of synthesis of amino-acids and in particular lysine in connection with the telomerisation reaction. As already stated, ααaω-tetrachloroalkanes, which have now become available, serve as the starting material for the preparation of various amino-acids. The following procedure has been proposed for the synthesis of lysine from ααaω-tetrachloropentane[6,7,211,212]:



The overall yield of lysine is 44%. It has also been suggested that ε-caprolactam be obtained from tetrachloropentane[213]:

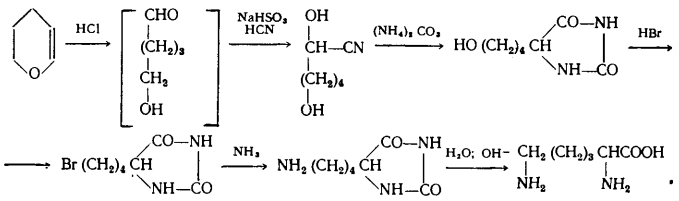


The ε-caprolactam is then converted into lysine, by the already known mechanism, via *N*-benzoylcaproic acid. One of the principal products of the telomerisation reaction of ethylene and trichloroacetic acid is ααω-trichlorocaproic acid — a new starting material for the synthesis of lysine. Hydrogen is substituted for one of the chlorine atoms in the α-position by hydrogenation and then the remaining α- and ω-chlorine atoms are replaced by amino-groups with the aid of potassium phthalimide:

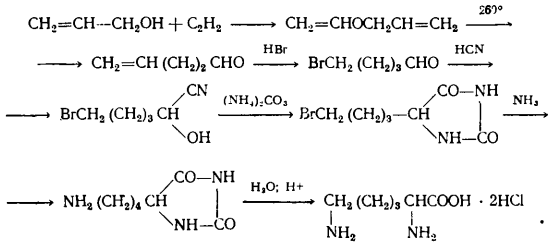


The yield of lysine is 53% with respect to the ester of ααω-trichlorocaproic acid. Simple ammonolysis is recommended for technical synthesis. This method undoubtedly merits attention in view of its exceptional simplicity and the availability of the starting materials[214].

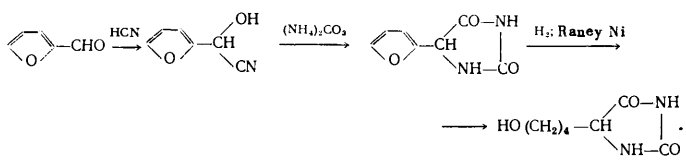
The oldest methods include the synthesis of lysine by the cyanohydrin method. Here one must mention the Gaudry method, which has also been studied by other investigators:



The initial dihydropyran is converted by the action of hot dilute hydrochloric acid into δ-hydroxyvaleric aldehyde, from which 5-(4-hydroxybutyl)hydantoin is obtained by treatment with hydrogen cyanide and ammonium carbonate. The next stages are replacement of the hydroxy-group by a halogen and ammonolysis; acid or alkaline hydrolysis complete the synthesis. The yield of the product is 30–40%.[215,216] Modifications of this method make it possible to obtain up to 51% of lysine[217]. The search for a readily available raw material for the preparation of the aldehyde component is being continued. Thus a patent describes the preparation of lysine (and other amino-acids) via vinyl ethers[218]:



5-(4-Hydroxybutyl)hydantoin can be obtained from the readily available furfural:

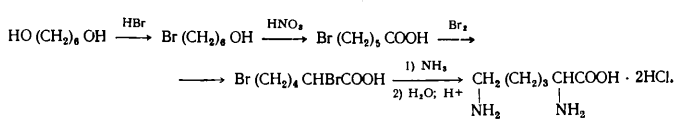


The hydantoin is then converted into lysine by the method described above. The total yield is 32%.[219]

Lysine can be obtained from piperidine in the following way. *N*-Chloropiperidine, formed when piperidinium acetate is acted upon by calcium or sodium hypochlorite, is dehydrohalogenated by booling with alcoholic alkali. The reaction product, the α-trimer of 2,3,4,5-tetrahydropyridine, is treated with ammonium carbonate, hydrogen cyanide, and water, lysine being isolated after purification on an ion-exchange resin[220].

Malonic ester synthesis has been widely used for the preparation of lysine. The use of malonic[221,222] and acetamidomalonic[223-225] esters has been described. δ-Bromovaleric acid[222], γ-chlorobutyronitrile[221], 1-bromo-4-chlorobutane[223], and acrolein[224,225] have served as components in these syntheses. The yields of lysine reach in some cases 30–40%[222] and even 55%.[223]

When hexane-1,6-diol is used as the starting material, it is possible to obtain lysine by the following simple operations:



The overall yield is 38%. The greatest difficulties in the synthesis are associated with the selective replacement of a hydroxyl by a halogen and the oxidation of the primary alcohol group to the carboxyl[227].

α-Aminogluconic acid can be converted into 5-hydroxylysine, the reduction of which gives lysine itself[228]. In the synthesis of lysine by the Finkbeiner method the chelate complex of 3-phenylhydantoin and methylmagnesium bromide can be alkylated with *N*-(4-bromobutyl)phthalimide[33,34].

Attempts have recently been made to obtain L-lysine by the Kolbe electrochemical reaction. A mixture of the monomethyl ester of *N*-phthaloyl-L-glutamic acid and *N*-phthaloyl-β-alanine was electrolysed in dimethylformamide. After appropriate treatment L-lysine was obtained in amounts which so far are only of theoretical importance[226].

In conclusion it is appropriate to mention that L-lysine for food and fodder additives can be obtained by combining chemical synthesis with stereospecific microbiological synthesis. For example, diaminopimelic acid prepared from ethoxydihydropyran is converted with the aid of *Bacillus sphaericus* into L-lysine. This method is also suitable for the separation of synthetic DL-lysine into optical isomers[229]. A combination of chemical and biological syntheses has been proposed by Ferris and coworkers. 2-Hydroxyiminoadipic acid is obtained by the hydrolysis of 5-cyano-2-hydroxyiminovaleric acid [synthesised from 2,6-di(hydroxyimino)-cyclohexanone]. This substance is added to a nutrient medium containing baker's yeast, lysine being isolated after fermentation[230].

Tryptophan

The chemical synthesis of tryptophan can be conveniently examined using the following classification of methods proposed by Hellmann in his review published in 1949.[231]

I. Syntheses from compounds containing the indole ring.

a. Condensation of indole-3-aldehyde with compounds containing an active methylene group.

b. Alkylation of esters of acylamino- and nitro-acids with gramine and diethylaminomethylindole.

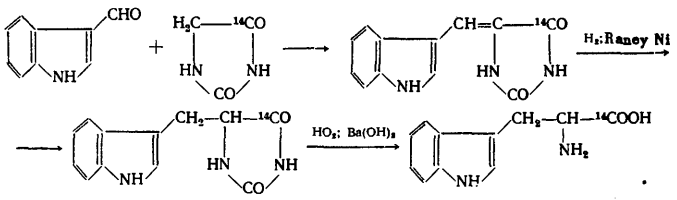
c. Alkylation of indole with various reagents.

II. Syntheses involving the formation of the indole ring.

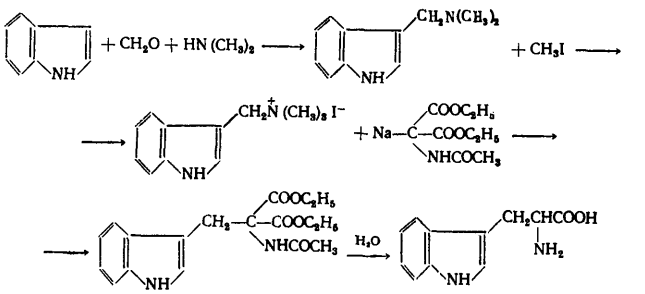
The syntheses of the first group, in particular the alkylation with gramine, have been studied extensively and are sufficiently simple for the preparation of tryptophan under laboratory conditions.

The preparation of tryptophan by the condensation of indole-3-aldehyde with benzoylglycine (the azlactone method) is

not used at the present time. The condensation of indole-3-aldehyde with hydantoin is used for the synthesis of tryptophan labelled at the carboxyl[232]:

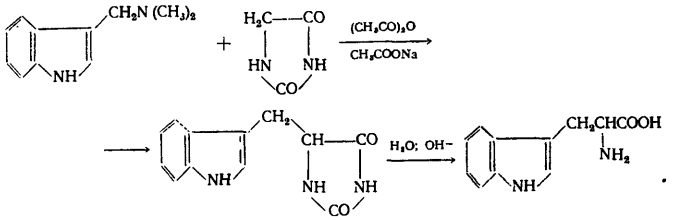


Gramine (dimethylaminomethylindole), obtained by the Mannich reaction from indole, formaldehyde, and dimethylamine, is widely used in tryptophan syntheses. For example, tryptophan can be obtained by the following reaction from acetamidomalonic ester and gramine[233,234]:

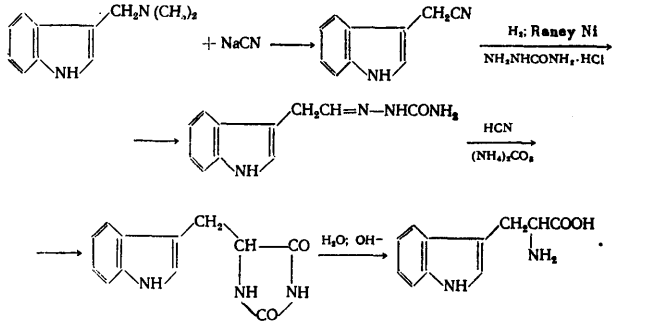


The yields of tryptophan reach 66% with respect to indole[235,236]. When formamidomalonic ester is used instead of acetamidomalonic ester and diethylaminomethylindole instead of gramine, the yield of tryptophan increases to 90%.[237] The following esters have also been alkylated with gramine in the same way (the percentage yields with respect to gramine are indicated in brackets): acetylcyanoacetic (71, with respect to indole)[83], acetamidoacetoacetic[238], acetoacetic (58)[239,240], cyanoacetic (22)[239], nitroacetic (45)[10,11], and nitromalonic (77)[19].

Gramine has been used in the synthesis of tryptophan hydantoin[241]:



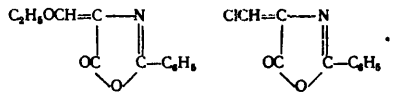
β-Indolylacetonitrile, obtained in quantitative yield by the alkylation of cyanide salts with gramine, serves as a new starting material in the synthesis of tryptophan:



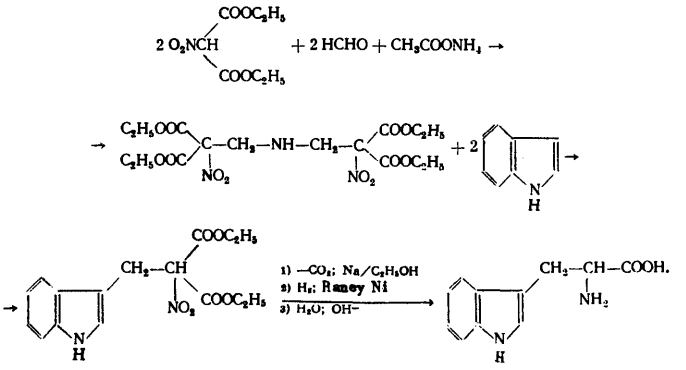
The semicarbazone of β-indolylacetaldehyde is prepared by the reduction of 3-indolylacetonitrile in the presence of semicarbazide. The semicarbazone is obtained as the *syn*-isomer, which on standing is converted into the more stable *anti*-isomer. The *syn*-isomer is more reactive and is converted into hydantoin in 66% yield, while the yield of hydantoin from the *anti*-isomer is 38%. The hydantoin is hydrolysed in the usual way and tryptophan is isolated in an overall yield of 33% with respect to gramine[242].

Gramine has been used as the alkylating agent in the preparation of tryptophan by the Finkbeiner method[33].

The procedures for the preparation of tryptophan in which indole is the starting material are simpler, since the necessity for the synthesis of gramine is eliminated. Alkylation of indole by a Mannich base derived from piperidine, formaldehyde, and formamidomalonic ester followed by hydrolysis and decarboxylation gives tryptophan in 71% yield[243]. A new method for the preparation of azlactones by the alkylation of indole with 4-ethoxymethylene-2-phenyl-5-oxazolone[244] and 4-chloromethylene-2-phenyl-5-oxazolone[245] makes it possible to obtain tryptophan in two stages with yields up to 75%:

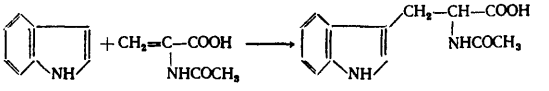


The key reaction in a new synthesis of tryptophan based on nitromalonic ester is the alkylation of indole with 1,1,5,5-tetraethoxycarbonyl-1,5-dinitro-3-azapentane — a Mannich base obtained from nitromalonic ester, formaldehyde, and ammonia:



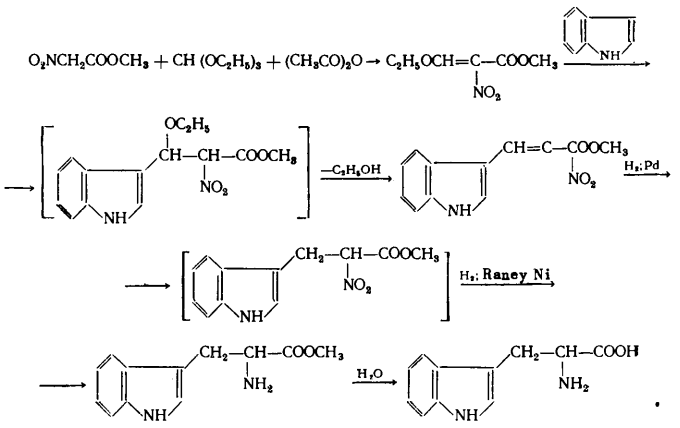
The decarboxylation, reduction of the nitro-group, and hydrolysis are carried out without isolating the intermediates. The overall yield with respect to indole is 50%.[20,21]

A simple method for the synthesis of *N*-acetyltryptophan in 57.7% yield consists in the addition of indole to α-acetamidoacrylic acid:

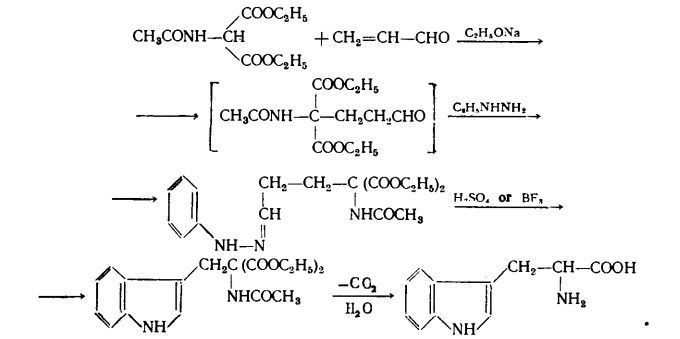


N-Acetyl-2-methyltryptophan and *N*-acetyl-7-methyltryptophan were obtained similarly[246].

Tryptophan has been obtained in 45% yield with respect to indole by an original method based on nitroacetic ester, using ethoxynitroacrylic acid as an intermediate[247]:

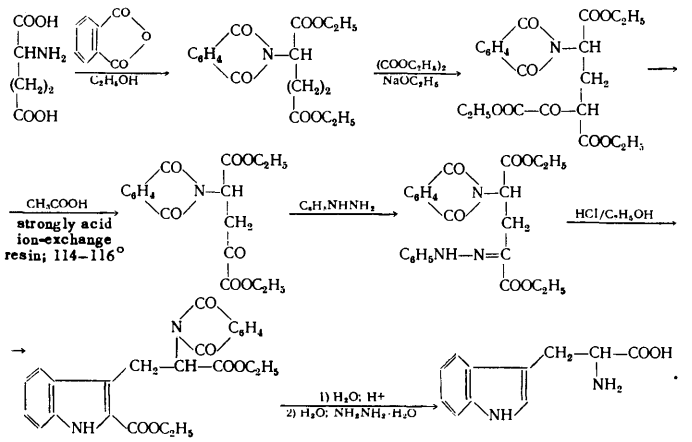


In all the cases examined the indole ring is introduced as such into the molecule, i.e. essentially each synthesis is only a partial synthesis of tryptophan. The Fischer reaction made it possible to perform the complete synthesis of tryptophan from starting materials not containing indole. The condensation of acetamidomalonic ester with acrolein must be regarded as the most successful procedure of this kind. The condensation product is treated with phenylhydrazine and the resulting phenylhydrazone is cyclised:



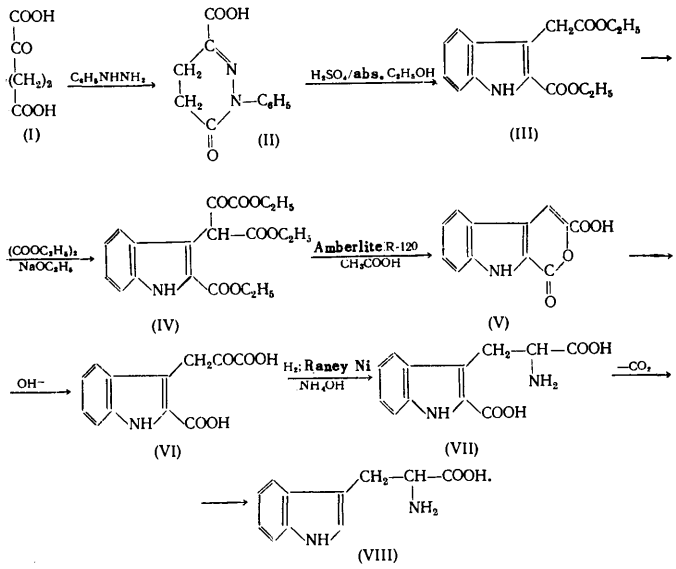
The overall yield with respect to acetamidomalonic ester is 43%.[248-250] Ion-exchange resins can be used as catalysts of the condensation of acrolein with acetamidomalonic ester and the cyclisation of phenylhydrazone[251].

In 1961 an attempt was made to prepare optically active tryptophan from optically active L-glutamic acid by the reaction

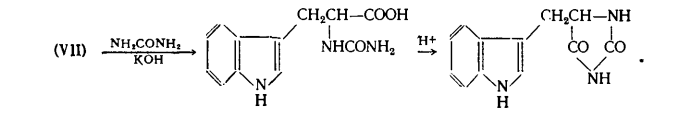


However, the attempt was unsuccessful, since racemisation takes place in the condensation with diethyl oxalate in an alkaline medium[252].

Another similar method is the synthesis of tryptophan from oxoglutaric acid, which includes seven stages with an overall yield of 35% (with respect to the initial acid)[253]:



A modification, starting with the conversion of the intermediate pyrone derivative (V), has been described in a patent[254]. Compound (V) is converted into β-(2-carboxy-3-indolyl)pyruvic acid (VI), which is reductively aminated to β-(2-carboxy-3-indolyl)-α-aminopropionic acid (VII). Further conversion of compound (VII) takes place by the mechanism



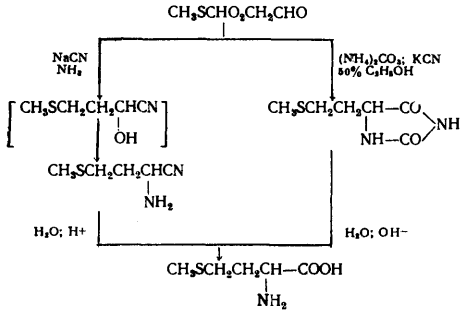
The hydantoin is hydrolysed and tryptophan is obtained in 50% yield. There is also a patent concerning the decarboxylation of compound (VII).[255] Tryptophan hydantoin can be obtained by the condensation of the phenylhydrazone of β-(hydantoin-5-yl)propionaldehyde. The latter was prepared by the reduction of 5-(β-cyanoethyl)hydantoin in the presence of phenylhydrazine[256,257].

Methionine

Methionine (α-amino-γ-methylthiobutyric acid) is the most important source of sulphur and plays an exceptionally important role in metabolism. The methods for the synthesis of methionine have not changed significantly in recent years. At the present time there are three fairly thoroughly developed procedures for the synthesis of methionine: (1) the cyanohydrin method; (2) syntheses with the aid of esters; (3) syntheses based on butyrolactone. The cyanohydrin method must be regarded as the most convenient and the most suitable for industrial manufacture. The starting material is β-methylthiopropionaldehyde which is obtained in good yield by the catalytic addition of methanethiol to acrolein[258,259]:

$$CH_3SH + CH_2{=}CHCHO \rightarrow CH_3SCH_2CH_2CHO$$

β-Methylthiopropionaldehyde is converted into methionine via an aminonitrile[258-263] or via hydantoin[250,259,264]:



If the reaction is performed at atmospheric pressure, the process via hydantoin gives best results (the total yield with respect to acrolein is 60%).[264] The application of pressure makes it possible to obtain in high yield α-amino-γ-methylthiobutyronitrile, the hydrolysis of which gives methionine. The yield of methionine is 82%,[260] but according to other data it is almost quantitative[262].

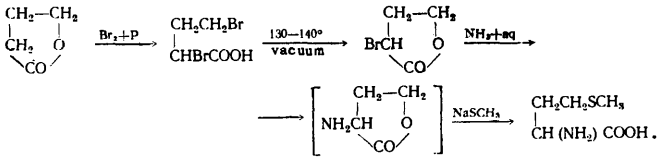
In the synthesis of methionine based on acetic and malonic ester derivatives α-chloro-β-methylthioethane, obtained from ethylene monothioglycol,

$$HSCH_2CH_2OH + (CH_3O)_2SO_2 \xrightarrow{OH^-} CH_3SCH_2CH_2OH \xrightarrow{SOCl_2} CH_3SCH_2CH_2Cl\ ,$$

is used as the alkylating agent. The yield varies from 70 to 90% depending on the purity of the starting material[265]. Acetamidocyanoacetic[68], phenylacetamidocyanoacetic[85], acetamidomalonic[266], formamidomalonic[267], and phthalimidomalonic[265,268] esters were alkylated with α-chloro-β-methylthioethane. The alkylated esters were then converted by simple operations (hydrolysis, decarboxylation) into the amino-acid, the yields varying from 24 to 60%.

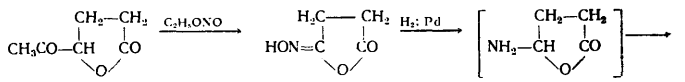
The phenylhydrazone of γ-methylthio-α-oxobutyric acid, obtained by the action of phenyldiazonium chloride on (β-methylthio)ethylcyanoacetic ester, gives a 49% yield of methionine on reduction with zinc in hydrochloric acid[89]. The ethyl ester of (β-methylthio)ethylcyanoacetic acid has been converted into methionine by the Darapskii method ($-COOC_2H_5 \rightarrow CONHNH_2 \rightarrow CON_3 \rightarrow NHCOOC_2H_5 \rightarrow NH_2$).[124]

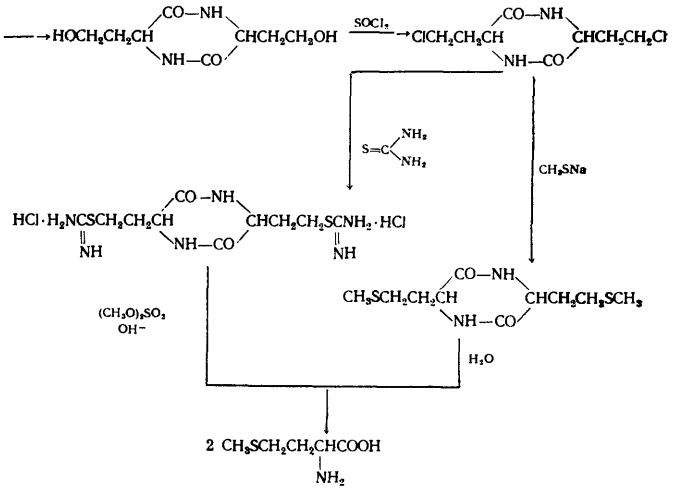
Butyrolactone can be converted into methionine in several ways. The simplest method includes four stages:



The total yield is 37%.[269]

In the free state α-amino-γ-butyrolactone readily dimerises with the formation of dioxopiperazine, which can serve as an intermediate in the synthesis of methionine:

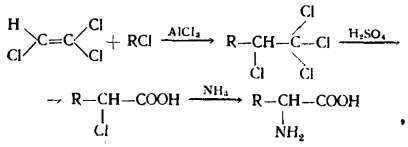




The total yield of the amino-acid when the methylthio-group is introduced with the aid of sodium methylsulphide amounts to 24% with respect to the butyrolactone[270]; 36% of methionine is obtained via the thiuronium salt[271]. α-Amino-γ-butyrolactone can be converted into α-amino-γ-hydroxybutyric acid and then into methionine by the halogenation of the hydroxy-group and the replacement of the halogen by CH_3S. The amino-group is protected by benzoylation[272] or the hydantoin is obtained[273].

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During the preparation of this review for printing, several papers on the synthesis of essential amino-acids were published. Baumgarten and coworkers continued the study of the general method for the preparation of α-amino-acids from imino-esters[274] which they proposed earlier[40]. A general method for the synthesis of α-amino-acids by the carboxylation and alkylation of hydantoin was put forward by Finkbeiner[275]. A new synthesis of DL-isoleucine and DL-valine from trichloroethylene and alkyl chlorides takes place as follows:



where R = $CH_3-CH-CH_3$ or $CH_3-CH-C_2H_5$. DL-Isoleucine and DL-alloisoleucine are obtained in a ratio of 35 : 65.[276]

Perekalin et al. suggest that the dihydrochloride of lysine be obtained from butadiene and nitroacetic ester. Butadiene is nitrohalogenated, the resulting halogenonitrobutene is alkylated with ethyl nitroacetate, and then the ethyl ester of 2,5-dinitrohex-4-enoic acid is reduced with hydrogen in the presence of acid palladium and hydrolysed with hydrochloric acid[277].

A new modification of the Akabori method[278] for the preparation of threonine was put forward. An increase in the amount of alkali used in the reaction made it possible to reduce the reaction time to 30 min and to reduce the temperature. The threonine : allothreonine ratio in the reaction product is 41 : 9, the overall yield of the diastereoisomers being 86%.

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CARBON SUBOXIDE IN ORGANIC SYNTHESIS

L.B. Dashkevich and V.G. Beilin

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I. INTRODUCTION

Carbon suboxide C_3O_2 (dioxoallene, dioxopropadiene), discovered by Diels in 1906, is a very unusual compound with four cumulative double bonds. The first investigations of Diels and coworkers [1] showed that it should be regarded as an internal dianhydride of malonic acid. Like methylene, carbon suboxide should be included, in principle, among the few "key compounds", and the study of its chemical properties will undoubtedly lead to the discovery of new and specific methods of organic synthesis.

Although carbon suboxide was actually discovered before keten, it has been much less investigated. Nevertheless malonic addition reactions occupy a fairly important position in practical organic chemistry. The malonyl radical is known to be incorporated in many biologically active compounds: barbiturates, pyrazolidinediones, substituted esters and amides of malonic acid, etc.

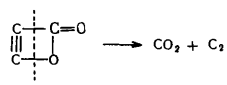
Nowadays, in the practical application of malonic addition reactions malonic acid, diethyl malonate, and malonyl dichloride are used. Compared with these compounds, carbon suboxide has a number of advantages, which consist in high yields of the desired products, their relative purity, and in the specificity of the reactions which take place only when carbon suboxide is used.

There exists no general review of the literature in which the reactivity of carbon suboxide with respect to various classes of chemical compounds is considered systematically. Grauer's review [2] published in 1960 covers the literature up to 1956 only and is far from complete. Of the earlier work, one may mention the paper of Vol'kenshtein [3], who more than thirty years ago drew attention to the promising possible applications of carbon suboxide. Recently carbon suboxide has been increasingly attracting the attention of investigators both in the Soviet Union and abroad.

The aim of the present article is to describe the present state of the chemistry of carbon suboxide, a knowledge of which may prove of interest to chemists working in the field of organic synthesis.

II. THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF CARBON SUBOXIDE

Until comparatively recently the structure of the C_3O_2 molecule remained controversial, which was to a large extent due to the difficulty of obtaining sufficiently pure carbon suboxide. Diels proposed the linear structure of 1,3-dioxopropadiene for carbon suboxide [1]. Most of the investigators working with carbon suboxide support this view, mainly on the basis of the methods of preparation of carbon suboxide — from malonic acid and its derivatives. Hypotheses have also been put forward that carbon suboxide can exist as the lactone of β-hydroxypropiolic acid [4]. Attempts were made to confirm this structure by the value of the dipole moment allegedly found for carbon suboxide [5], and also by its thermal decomposition to C_2 and CO_2: [6]



These views are in conflict with the molar refraction and molar dispersion of carbon suboxide [7,8].

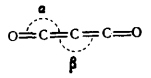
Numerous electron diffraction [9-12] and spectroscopic studies in the last decades established that carbon suboxide has an acyclic structure [13]. Infrared and Raman spectra [13-22] and also its ultraviolet spectra [23] have been investigated. The interatomic distances and the valence angles in the suboxide molecules were calculated from these data:

C=C	C=O
1.28±0.15Å	1.16±0.015Å

Thus the C=C bond in carbon suboxide is shorter than in alkenes (1.34 Å) and in keten (1.32 Å). [24] The length of the C=O bond is close to the interatomic distance in the carbonyl group of keten (1.17 Å) and in chloro- and fluoro-carbonyl compounds (1.18 and 1.17 Å), [25,26] but differs significantly from the length in aliphatic ketones (1.22–1.24 Å). [26]

Vol'kenshtein [27], who explained this shortening of the interatomic distance by the pronounced displacement of the electron cloud towards the oxygen atoms, suggested that the C_3O_2 molecule be represented thus: O=C=C=C=O.

While the interatomic distance data can be regarded as adequately reliable, the problem of the steric disposition of the atoms in carbon suboxide remained controversial until very recently. The following values have been calculated for the valence angles:



180±10°	180±10°	[11]
180°	158°	[14]
180°	180°	[15]

Data suggesting the presence of a dipole moment in carbon suboxide [5] and also calculations of the force constants of the molecule [28,29] suggested a zigzag structure (symmetry group C_{2h}). However, the study of the infrared spectra of carbon suboxide in various states of aggregation [18] and also the study of their fine structure [18,20,22] indicate a linear structure for the C_3O_2 molecule (point symmetry group $D_{\infty h}$). Earlier data [5], indicating a dipole moment of 0.7 D in carbon suboxide, were probably obtained in consequence of the presence of an admixture of keten [12,30].

Some of the physicochemical characteristics of carbon suboxide are as follows. At the normal temperature carbon suboxide is a gas with a sharp specific smell.

B.p. + 6.8°C (Refs. 31,32); m.p. −107°C (Ref. 33)
−108°C (Ref. 34)
−111.3°C (Ref. 35)
−112.5°C (Ref. 36)
Vapour pressure at 0° 567–568 mmHg (Ref. 31)

$n_D^0 = 1.45538$ (Ref. 7).

There are no reliable data in the literature on the heat of formation of carbon suboxide. The following values may be quoted

$\Delta H_f(C_3O_2)$ = 47.7 kcal mole^{-1} (Ref. 37)
55.0 kcal mole^{-1} (Refs. 38,39)
18.0 kcal mole^{-1} (Ref. 4)
8 ± 5 kcal mole^{-1} (Ref. 40)
Dissociation energy D_0 = 635.234 kcal mole^{-1} (Ref. 40)
Molar heat of combustion of C_3O_2 = 234.6 kcal mole^{-1} (Ref. 37), 300 kcal mole^{-1} (Ref. 6).

Tables of the thermodynamic functions of carbon suboxide at temperatures up to 2000°K [22] and 6000°K [40] have been set up.

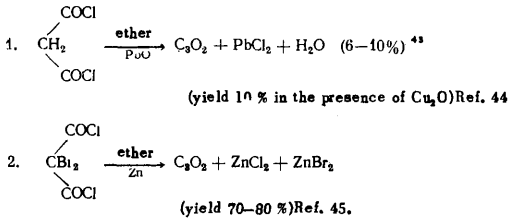
Carbon suboxide is soluble in the majority of organic solvents. Ethyl ether, tetrahydrofuran, and dioxan are especially often used in practice. It is a very toxic compound. Even at low concentrations it acts as a powerful lachrymator and at high concentrations causes asphyxiation. It has been established that carbon suboxide is a powerful blood poison (its effect on haemoglobin is analogous to that of carbon monoxide). The maximum permissible concentration of carbon suboxide in a dry atmosphere is 0.2–0.4%. [41]

III. METHODS OF PREPARATION

A fairly large number of reactions are known in which the formation of carbon suboxides is observed. However, only some of them are of practical importance. All the known methods can be arbitrarily divided into two groups. (a) preparations based on malonic acid and its derivatives (the structure of the carbon skeleton is retained in the process); (b) pyrolysis of β-dicarbonyl compounds which involves degradation of the carbon skeleton.

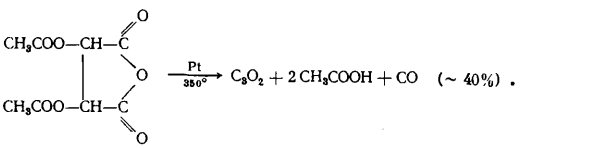
a. Diels was the first to obtain carbon suboxide on heating diethyl malonate with phosphorus pentoxide [1]. Subsequently the ester was replaced by malonic acid itself. In the latter case the yield of carbon suboxide amounted to 18–20% after a number of improvements [7,33,42]. The maximum yield of carbon suboxide from diethyl malonate was obtained by Korshak and coworkers (30–37%). [34]

Staudinger proposed two methods for the synthesis of carbon suboxide:



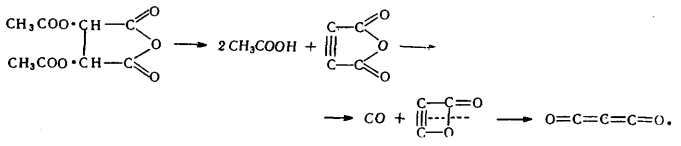
So far an 80% yield of carbon suboxide has been obtained only by the second method. However, an important disadvantage of this method is that carbon suboxide is not obtained in a free form but in ethereal solution. This restricts the scope of the method. Furthermore, the synthesis of the starting materials is relatively complex and very time-consuming. Another disadvantage of this entire group of methods for the synthesis of carbon suboxide is that malonic acid and its derivatives are used as the starting materials, and they themselves are capable of "malonylation". For this reason, the second group of reactions is of considerable interest.

b. The most practical method for the preparation of carbon suboxide proved to be the pyrolysis of the anhydride of diacetyltartaric acid, proposed by Ott and Schmidt [46]:



Subsequently Hurd and Pilgrim showed that the high-temperature non-catalytic pyrolysis of the anhydride leads to approximately the same results (quartz tube, 750°). [47]

The following mechanism has been proposed for the synthesis of carbon suboxide from the anhydride of diacetyltartaric acid:



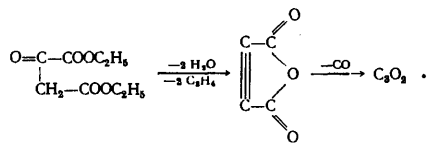
This mechanism of the pyrolysis is confirmed by the formation of carbon suboxide in the pyrolysis of acetylenedicarboxylic acid under analogous conditions [48] and also by the absence of radioactivity from the carbon suboxide obtained from the anhydride of acetyltartaric acid labelled with ^{14}C in the acetyl groups [48,49].

The technique of the pyrolysis has undergone various modifications. For example, it has been suggested that sand be used instead of mercury to force the acetyltartaric acid anhydride melt from the burette into the pyrolysis tube [50]. Later it was shown that it is more convenient to use the anhydride of diacetyltartaric acid in acetic anhydride [48].

Various data have been quoted for the temperature conditions of the pyrolysis and the yields: 625–650°C (40–49%);[47] 570–600°C (41%);[51] 700–725°C (40%);[48] 700–750°C (43–46%).[52]

A large number of dicarbonyl compounds have been pyrolysed in connection with research into new reactions involving the formation of carbon suboxide. Carbon suboxide forms in the pyrolysis of lactic acids, succinic acid derivatives, acetylenedicarboxylic acid and its esters, certain β-keto-esters, etc.[48,53,54] Among the reactions investigated, only the pyrolysis of diethyl oxaloacetate (yield 48%)[48] is of practical importance.

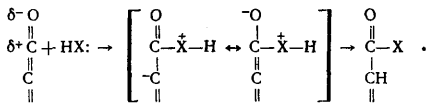
In the pyrolysis of diethyl [4-^{14}C]oxaloacetate it proved possible for the first time to obtain carbon suboxide labelled with ^{14}C. The molecular radioactivity (MR) of carbon suboxide was found to be smaller by a factor of two than that of the initial diethyl oxaloacetate. This shows that the 1-^{12}C and 4-^{14}C atoms of the carbon skeleton of oxaloacetic acid participate in the decarboxylation to an equal extent. This finding suggests that the process proceeds similarly to the pyrolysis of the anhydride of diacetyltartaric acid[48]:



The formation of carbon suboxide has also been observed on passing a weak electric discharge through carbon monoxide[56] or a mixture of carbon monoxide and carbon dioxide[57] in an ozoniser ($4CO \rightarrow C_3O_2 + CO_2$) and on irradiating a mixture of carbon monoxide and carbon dioxide with ultraviolet light[57].

IV. CHEMICAL PROPERTIES OF CARBON SUBOXIDE

The first investigators of carbon suboxide already noted its unsaturated character and tendency towards addition reactions. At the present time the most thoroughly investigated reactions of carbon suboxide are those with various nucleophilic reagents: amines, alcohols, mercaptans, etc. It must be supposed that in this case the addition begins with the penetration of the unshared electron pair of the nucleophilic reagent into the electron gap of the extreme carbon atom of carbon suboxide:



The proton can add either to the oxygen or the carbon atom. In the first case the unstable enol isomerises to the carbonyl form. The fact that addition to oxygen is possible is confirmed, for example, by the participation of carbon suboxide in organometallic synthesis[60].

While the mechanism of addition to ketones has been frequently discussed in the literature[58,59], the same process involving carbon suboxide has been almost entirely neglected[60]. There is hardly any point in considering the problem of whether addition takes place at the carbonyl or ethylene bond, since the extreme carbon atom of carbon suboxide is simultaneously a carbonyl and an ethylenic atom. In any case, it is the atom subject to primary nucleophilic attack.

1. Reactions with Hydroxy- and Mercapto-Compounds

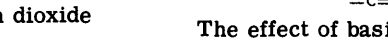
Carbon suboxide reacts with water and alcohols, forming malonic acid and its esters respectively:

$$2\,ROH + O{=}C{=}C{=}C{=}O \rightarrow ROCOCH_2COOR\ .$$

At room temperature the reaction of carbon suboxide with water is fairly slow but is accelerated at 60–70°C in the presence of catalytic amounts of hydrochloric acid. The yield of malonic acid is quantitative[61]. This reaction has been used to prepare 4-D-malonic acid. On carrying out the reaction of carbon suboxide with deuterium oxide in solution in benzene[62] or carbon tetrachloride[63], deuteriated malonic acid was obtained. On the other hand, when the reaction was carried out in deuterium oxide at 50°C, the final product was only deuteriated acetic acid[64].

Methyl and ethyl alcohols react with carbon suboxide even at room temperature. Starting with propyl alcohol, heat and catalysts are required[61]. Phenol reacts only in the presence of catalysts[61,65]. Nitro-alcohols can be "malonylated" with the aid of carbon suboxide only when aluminium chloride is used as the catalyst[50]. Reactions of carbon suboxide with hydroxylamine and oximes, involving the mechanism common to hydroxy-compounds, have been described[47,66].

In the reaction with hydroxy-compounds acid catalysts were mainly used: sulphuric acid, *p*-toluenesulphonic acid[65], and hydrogen chloride[61]; their role probably consists in the additional polarisation of the carbonyl group of carbon suboxide and hence in an increase of the electrophilicity of the carbonyl carbon:



The effect of basic catalysis on addition reactions of carbon suboxide has not been considered, although some experiments on those lines have been performed. Hegar[51] carried out the reaction of carbon suboxide with aqueous solutions of phenol and butanol in the pH range 1–14 at 0°C. Under these conditions he obtained exclusively the phenyl ester of malonic acid, the maximum yield occurring at pH 11. It has recently been established that in the reaction of carbon suboxide with alcohols the corresponding alkoxides are good catalysts. The yield of malonate esters is then nearly quantitative[67]. We believe that both these findings confirm the applicability of basic catalysis to reactions of carbon suboxide with weak nucleophilic reagents, in which there is a possibility of the formation of an anion with much more pronounced nucleophilic properties.

With diols carbon suboxide forms polyesters, the molecular weight of which is several thousands[34,52]. Carbon suboxide reacts fairly readily with formic and acetic acids, mixed anhydrides of malonic acid being formed[42]. The reaction of carbon suboxide with anhydrous oxalic acid is accompanied by the evolution of carbon monoxide and dioxide and leads to the formation of the lactone of β-hydroxyisopropylmalonic acid, a solid product, whose structure has not been established, being produced with malonic acid[18,66].

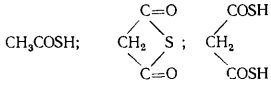
Mercaptans react with carbon suboxide under somewhat more severe conditions than do alcohols. The corresponding esters of dithiomalonic acid are formed[52]:



However, when diethylaminoethanol and diethylaminoethanethiol are "malonylated" with the aid of carbon suboxide the

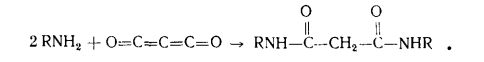
reaction takes place much more readily with the mercaptan[69]. These data are satisfactorily consistent with analogous work in the chemistry of keten[58] and also with work on the introduction of the malonyl acid group into proteins with the aid of carbon suboxide[70], which can probably be accounted for by the marked nucleophilic properties of the SH group[71].

Depending on the relative amounts of the reagents, the reaction of carbon disulphide with carbon suboxide gives rise to a number of compounds[68,72]:



2. Reactions with Primary Amines

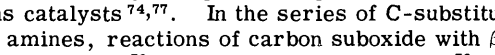
In consequence of their pronounced nucleophilic properties, amines react extremely readily with carbon suboxide:



This group of reactions of carbon suboxide has been investigated more thoroughly than others, which makes it possible to follow at least qualitatively the effect of the properties of the amine on its reactivity with respect to carbon suboxide. Since carbon suboxide is a Lewis acid and amines are bases, the reaction can be regarded as an acid–base process. Then the basicity of the amine can be regarded as a criterion of its reactivity. This makes it possible to estimate to some extent the effect of substituents in the amine on the course of the reaction[73].

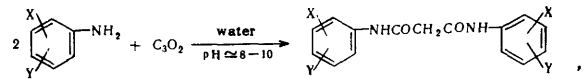
Unsubstituted primary amines. These react with carbon suboxide under mild conditions and with almost quantitative yields. The reaction is a rule performed in an indifferent solvent at the normal temperature or below 0°C. The reactions of carbon suboxide with acyclic, alicyclic, and aromatic amines have been investigated[74,75]. As was to be expected, the phenyl group lowers somewhat the rate of reaction, which, however, does not prevent the use of the reaction between carbon suboxide and aniline for the quantitative determination of the latter[48].

Substituted primary amines. Pauw[74] showed that the reaction of carbon suboxide with *o*-, *m*-, and *p*-alkylanilines, -halogenoanilines, and -alkoxyanilines results in high yields of the corresponding malonic acid diamides[76]. On introduction into the benzene ring of electrophilic substituents, the reduction of the basicity of the amine becomes so appreciable that, for example, *o*-, *m*-, and *p*-aminoacetophenones and aminobenzoic acid esters virtually do not react with carbon suboxide in the absence of catalysts[75]. The reaction of carbon suboxide with *o*- and *p*-sulphoanilines and *o*- and *p*-nitroanilines could not be achieved even on prolonged heating and in the presence of various catalysts[74,77]. In the series of C-substituted aliphatic amines, reactions of carbon suboxide with β-substituted ethylamines[78], βγ-halogenopropylamines[79], and amino-acids and their esters[74,78,80,81,82] have been carried out:



where X = Cl, Br, OH, OR, SH, SR, ArC=O, COOR, COOH, C≡N, and CH_2=(allylamine).

The acylation of amines with carbon suboxide is as a rule performed in an organic solvent. However, as a result of the difference between the rates of the reactions of amines and water, it is in many cases possible to use water successfully as the reaction medium[77]:

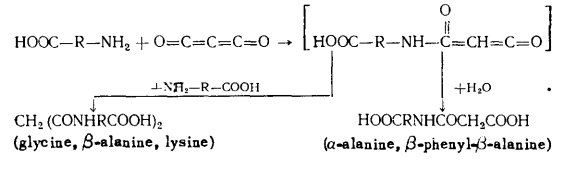


where

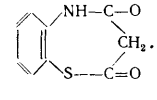
X	*o*-, *m*-, *p*-COOH	*o*-, *m*-, *p*-OH	*m*-, *p*-COOH
Y	H	H	*p*-, *m*-OH

The "malonylation" of halogenoalkylamines (β-chloroethylamine, etc.), which are unstable in the form of the free bases, takes place with high yields when the base is produced from the aqueous solution of its salt by adding alkali during the reaction[78].

Aliphatic amino-acids also readily react with carbon suboxide in aqueous media at pH 8–10.[78,80,81,82]. However, when α-alanine and β-phenylalanine were "malonylated", it proved possible to isolate from the reaction medium only the monoamides of malonic acid[73,78]. It should be noted that the formation of monoamides has been observed in the acylation of amino-acids in which the amino-group is linked to a secondary carbon atom. This course of the reaction may be associated with the fact that the presence of the substituent (methyl or phenyl) gives rise to steric hindrance to the reaction of the intermediate aldoketone with a second amino-acid molecule. As a result, the rates of the reactions with a second amino-acid molecule and water become comparable:



When the C-substituent of the amine is itself reactive with respect to carbon suboxide (OH, SH), it may be expected that the reaction will take place in several ways. However, whereas, as stated above, β-hydroxyethylamine and β-mercaptoethylamine, which are fairly strong bases, react with carbon suboxide via the amino-group, in reactions involving the "malonylation" of *o*-aminothiophenol, in which the basicity of the amino-group is greatly reduced, a cyclic addition product (2,3-benzo-1-thia-4-azacycloheptane-5,7-dione) is obtained[73,83]:



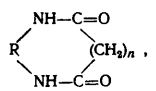
Secondary amines. As a result of their high basicity, it would seem that these should react with carbon suboxide fairly readily in accordance with the general mechanism. However, Pauw[74] failed to identify the products of the reaction of carbon suboxide with dimethyl- and diethyl-amines. Subsequently this reaction ceased to attract the attention of investigators. The reaction of carbon suboxide with secondary cyclic amines (cyclic imines) has been more widely investigated. Ethyleneimine reacts with carbon suboxide, giving *NN'*-malonylbisethyleneimine in good yield only in "absolute" ethyl ether between -60° and -70°C.[64] At higher temperatures there is a possibility of the formation of polymeric products[51]. It is noteworthy that attempts to "malonylate" ethyleneimine by the usual method (malonyl dichloride in the presence of triethylamine

in benzene) proved unsuccessful[85]. Higher polymethyleneimines, up to heptamethyleneimine inclusive, also react fairly readily with carbon suboxide; the yields of products range from 60% up to quantitative[84,86]. When the reaction is performed in the presence of water, there is a possibility of the formation of *N*-acetyl derivatives. Thus in the "malonylation" of ethyleneimine the formation of a product undergoing rapid decomposition, possibly *N*-acetylethyleneimine, was observed[51,73], the yield of *N*-acetylpiperidine being 82%.[86]

Substituted oxazolidines and thioazolidines react with carbon suboxide similarly[83,87]. The yields range from 50 to 80%, thiazolidine and 2,2-dimethylthiazolidine undergoing "malonylation" even in an aqueous medium. All these compounds are fairly strong bases ($pK_b < 10$). With still less basic amines ($pK_b > 10$), for example benzo-condensed heterocycles, the reaction is carried out in the presence of catalysts — sulphuric acid[51] and aluminium chloride[73,84]. Under these conditions 1,2,3,4-tetrahydroquinoline reacts with carbon suboxide fairly rapidly, the yield of products being 72%,[84] while without catalysts the yield of *NN'*-malonylbistetrahydroquinoline is only about 30% and the reaction takes several days[88]. Diethyl malonate also reacts in the presence of aluminium chloride but under more severe conditions. The product is 1,8-malonyl-1,2,3,4-tetrahydroquinoline[89].

Tertiary amines. Diels and Hansen[72] showed that quinoline, codeine, nicotine, and certain other heterocyclic compounds with a tertiary nitrogen atom react with carbon suboxide, forming coloured products of unknown structure. The powerful catalytic action of tertiary amines (particularly pyridine and triethylamine)[51] on the polymerisation of carbon suboxide has been frequently noted. Quaternary ammonium bases have a similar effect[51].

Diamines. In contrast to diols, these react with carbon suboxide, forming either linear polyamides or cyclic diamides, depending on the reaction conditions. When the reaction was carried out in ethereal solutions with gradual addition of carbon suboxide to the reaction mixture, cyclic addition products were obtained even with hexa- and deca-methylenediamines[74,90,91]:

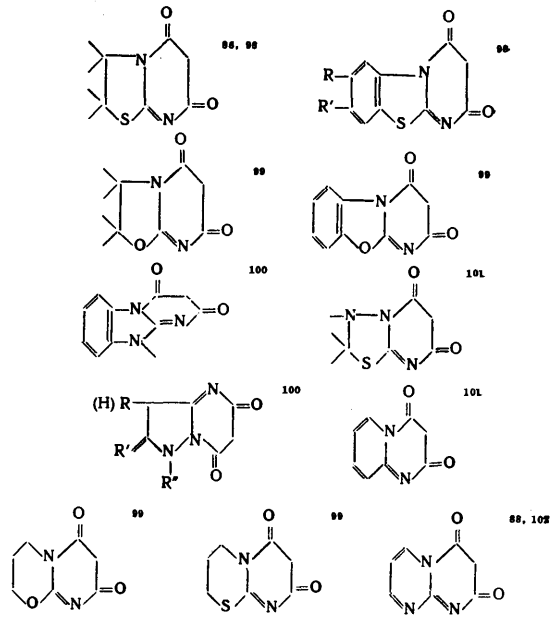


where R = $(CH_2)_n$ with n = 2–6 and 10. Under more severe conditions (heat, pressure), the products are polyamides[34,51]:

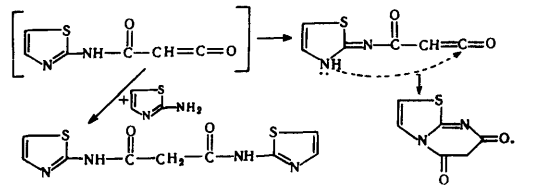
$$[-NH-RCOCH_2CO-]_n,$$

where R = $(CH_2)_6$ and $(CH_2)_{10}$.

Amino–imino tautomers. Recently the capacity of carbon suboxide to react with compounds capable of amino–imino tautomerism with formation of various heterocyclic systems condensed with 2,4-dioxopyrimidine has been attracting much attention. Syntheses of heterocyclic systems of this kind using malonic ester and malonyl dichloride have been described, but the reactions often require severe conditions[92–95]. In certain cases, when diethyl malonate is used as the "malonylating" agent, only linear acylation products were obtained[93], while carbon suboxide gives cyclic products, for example with 2-aminothiazole[88,96,97]. The study of the reaction of carbon suboxide with a number of amino–imino tautomers led to the synthesis of the following heterocyclic systems[88,98–102]:

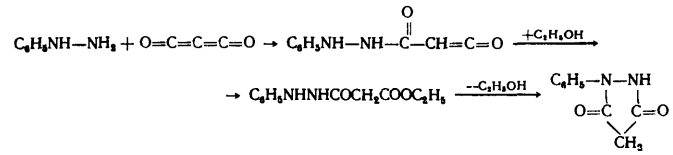


In the reaction involving the introduction of the malonyl group with carbon suboxide into certain amino–imino tautomers it was noted that the formation of cyclic products is accompanied by the formation of linear malonic acid diamides. Thus in the reaction of carbon suboxide with 2-aminothiazole the yields of the cyclic and acyclic products were 42.5 and 57.5% respectively[103]. Only the linear diamides were obtained in the reaction of carbon suboxide with 3-aminopyrazoles[100]. This course of the reaction can be satisfactorily explained by the different degrees of aromaticity of the initial heterocycles and hence their different capacities for isomerisation and cyclisation in the stage involving the formation of the intermediate aldoketen:



3. Reactions with Hydrazine and its Derivatives

The first studies on the reaction of carbon suboxide with hydrazines were performed by Van Alphen[90]. The aim was to prepare pyrazolidine-3,5-dione. However, with hydrazine itself, a polymeric product, probably of a linear structure, was obtained. Initially it was possible to obtain a cyclic addition product only with *N*-phenylhydrazine. The reaction proceeds through a stage involving the formation of *N*-malonylphenylhydrazine, the cyclisation of which yields 1-phenyl-3,5-dioxopyrazolidine. This mechanism of the reaction has been confirmed by other workers[91]:



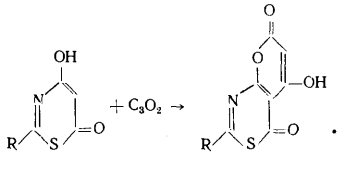
Later Van Alphen also obtained a series of 1,2-disubstituted 3,5-dioxopyrazolidines via carbon suboxide [104]. Reactions leading to the formation of 3,5-dioxopyrazolidines are also known for other "malonylating" agents (malonyl dichloride, diethyl malonate) [105,106], but yields are fairly low.

Reactions of carbon suboxide with substituted hydrazines [107,108] and hydrazobenzene [108] have been described comparatively recently. It has been stated that the reactions can take place without catalyst at temperatures close to 0°C. In the reaction of carbon suboxide with unsubstituted pyrazolidine cyclic addition of carbon suboxide with formation of 1,2-(3,5-dioxopyrazolidino)pyrazolidine also takes place [109].

4. Reactions with Amides and Diamides

It was believed that, in view of their greatly reduced basicity, amides are unreactive with respect to carbon suboxide. However, Ziegler [88] showed that the reactions of benzamide and 3,4-dimethylbenzamide with carbon suboxide on heating for several hours at 60–80° in tetrahydrofuran give bismalonyl derivatives in 65% yield. The reaction with the amides of thioacids takes place in a different way. In contrast to the usual amides, they react in the thiol form with formation of 2-substituted 4-hydroxy-1,3--thiazin-6-one. [88,110]

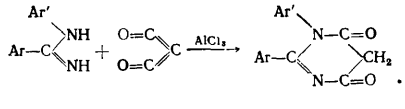
According to Ziegler, on heating with an excess of carbon monoxide, there is a possibility of further addition of carbon suboxide with formation of hydroxypyrone structures, which in turn can again combine with carbon suboxide:



Diamides (urea and thiourea) are acylated with carbon suboxide to barbituric and thiobarbituric acids. Van Alphen observed this only with the aid of qualitative reactions for barbituric acid [90], but after improvement of the method the yields reached 75–85% [91,110] and 56%. [91] *N*-Acetylthiourea reacts in the thiol form with formation of 2-acetyl-4-hydroxy--1,3-thiazin-6-one (yield 90%). [110]

5. Reactions with Amidines

The interaction of carbon suboxide with amidines in which the basicity of the NH groups is approximately the same (for example, with an *N*-arylbenzamidine) leads to the formation of high yields of 1,2-aryl-4,6-dioxotetrahydropyrimidines [111–114]:



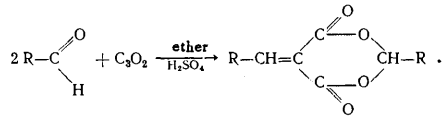
Unsubstituted amidines can react with carbon suboxide according to different mechanisms. Benzamidine reacts with carbon suboxide only via one amino-group, forming *NN'*-malonylbisbenzamidine, while *p*-toluamidine reacts via the amino- and imino-groups, yielding 2-(*p*-tolyl)--1,6-dioxotetrahydropyrimidine [112]. The use of malonyl dichloride [115] and dialkyl malonates [116,117] in these syntheses instead of carbon suboxide results in lower yields.

6. Reactions with Schiff Bases

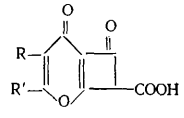
The study of these reactions was undertaken with the aim of preparing azetidine-2-ones containing an active keten grouping, which would make possible their use in the synthesis of biologically active substances with β-lactam rings. However, the reaction of carbon suboxide with benzylideneaniline takes place only under severe conditions (heating to 200°) which leads to the autocondensation of the intermediate aldoketen; only a complex compound with cyclobutane rings forms [118].

7. Reactions with Carbonyl Compounds

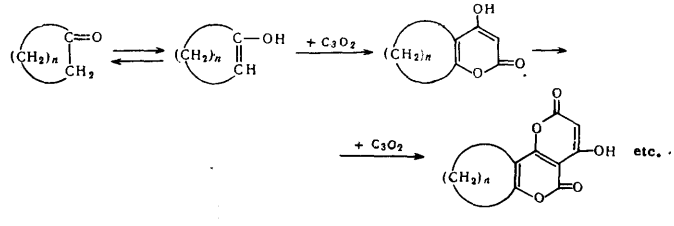
While keten readily reacts with aldehydes to form β-lactones [120], carbon suboxide behaves in a different way in reactions with aldehydes [51,119]. The reactions have been performed with benzaldehyde, *p*-toluic aldehyde, *p*-chlorobenzaldehyde, and cinnamaldehyde. In all cases high yields were obtained of the arylidene esters of substituted malonic acids, whose structure was demonstrated by synthesis and by infrared spectroscopy:



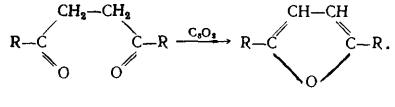
On reaction with carbon suboxide, β-diketones and β-keto-esters form compounds with the general formula [121]:



The probable mechanism of this reaction is the interaction of carbon suboxide with the enol form of the dicarbonyl compound and the subsequent addition of a second carbon suboxide molecule to the hydroxypyrone. A similar addition of carbon suboxide to cyclic ketones, which tend to enolise if only to a slight extent, has been described by Ziegler [88]. However, he also attributes the cyclopyrone structure to products of further addition of carbon suboxide:



Like keten [118], in reactions with γ-diketones carbon suboxide behaves as a dehydrating agent, which leads to the closure of the furan ring [51]:



8. Carbon Suboxide in the Friedel–Crafts Reaction

In the presence of equimolar amounts of anhydrous aluminium chloride carbon suboxide enters into the Friedel–Crafts reaction with benzene, naphthalene, and their homologues [122,123], with formation of aryl methyl ketones:

$$ArH + C_3O_2 \rightarrow [R{-}COCH{=}C{=}O] \xrightarrow[-CO_2]{+H_2O} Ar{-}\overset{\overset{O}{\|}}{C}{-}CH_3 .$$

Although it proved impossible to isolate the intermediate aldoketen, convincing proof of its existence has been secured. Without preliminary hydration, the reaction mixture with benzene was treated with aniline or absolute alcohol. Benzoylacetanilide and ethyl benzoylacetate were then isolated [124]:

$$\left[\begin{matrix}O\\ \|\\ C_6H_5{-}C{-}CH{=}C{=}O\end{matrix}\right] \begin{matrix}+ C_6H_5NH_2 \rightarrow C_6H_5COCH_2CONHC_6H_5\\ + C_2H_5OH \rightarrow C_6H_5COCH_2COOC_2H_5 .\end{matrix}$$

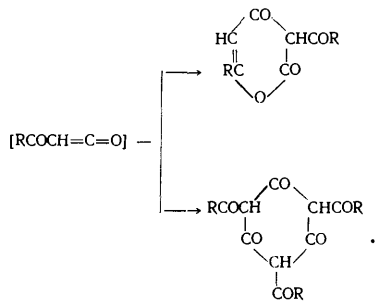
9. Reactions with Organometallic Compounds

The participation of carbon suboxide in organomagnesium [125-128] and organolithium [129] syntheses has been described. Depending on the reaction conditions and the relative amounts of the reactants, β-diketones [127,129] or methyl ketones [125,126,128] can be obtained:

1. $C_3O_2 + 2\,Mg\begin{matrix}R\\X\end{matrix} \rightarrow XMgO{-}\overset{R}{\underset{|}{C}}{=}C{=}\overset{R}{\underset{|}{C}}{-}OMgX \xrightarrow{2H_2O} R(OH)C{=}C(OH)R \rightarrow$
$\rightarrow RCCOCH_2COR$

2. $C_3O_2 + Mg\begin{matrix}R\\X\end{matrix} \rightarrow XMgO{-}\overset{R}{\underset{|}{C}}{=}C{=}O \xrightarrow[-CO_2]{H_2O} R{-}COCH_3 .$

It has been shown [125,126] that the intermediate aldoketen can react further by another mechanism with formation of cyclic dimers and trimers:



The capacity of carbon suboxide to enter into the Reformatskii reaction has been demonstrated by Dashkevich and Siraya [130]:

$$Zn + BrCH_2COOC_2H_5 + C_3O_2 \rightarrow C_2H_5OCOCH_2{-}C(ZnBr){=}C{=}O \xrightarrow{H_2O} \rightarrow C_2H_5OCOCH_2{-}COCH{=}C{=}O.$$

Since it proved impossible to isolate the aldoketen, the latter was hydrated, decarboxylated, and the acetoacetic ester obtained was subjected to ketone decomposition:

$$C_2H_5OCOCH_2COCH{=}C{=}O \xrightarrow{H_2O} C_2H_5OCOCH_2COCH_3 \rightarrow CH_3COCH_3 + CO_2 + C_2H_5OH.$$

Data on the reaction of carbon suboxide with sodium alkoxides in the corresponding alcohol [67] were presented above.

It has been shown that, as the size of the alcohol radical increases, there is a corresponding increase in the amount of the sodium derivative of the dialkyl malonate formed:

$$RONa + C_3O_2 \rightarrow ROCOCNa{=}C{=}O \xrightarrow{HOR} ROCOCHNaCOOR,$$

where R = C_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}, and C_8H_{17}. With ethyl and methyl alcohols, dialkyl malonates were obtained exclusively.

10. Reactions with Halides and Oxidation and Reduction of Carbon Suboxide

The addition of hydrogen halides to carbon suboxide results in the formation of malonyl halides [1]. From the reaction with ClBr in carbon tetrachloride the dichloride of dibromomalonic acid was isolated [124].

The oxidation and reduction of carbon suboxide have virtually not been investigated. In the attempt to reduce carbon suboxide with molecular hydrogen on nickel or palladium a mixture of products, consisting mainly of propene, together with acetic acid and small amounts of propane and water, was obtained [131] instead of the expected reduction products — propane-1,3-diol or propane.

According to the results of Staudinger, who studied the oxidation of ketens, carbon suboxide does not react with oxygen [132]. On cautious oxidation of carbon suboxide with a 2% solution of potassium permanganate, it proved possible to isolate a small amount of mesoxalic acid, which was identified via its phenylhydrazone [73]:

$$O{=}C{=}C{=}C{=}O \xrightarrow{2\%\ KMnO_4} \underset{OH}{\overset{O}{C}}{-}\underset{OH}{\overset{OH}{C}}{-}\overset{O}{C} .$$

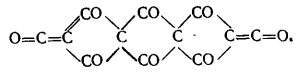
11. Polymerisation of Carbon Suboxide

The polymerisation of carbon suboxide was first observed by Diels [1]. The polymer which he described consisted of an amorphous powder whose colour ranged from dark red to black and which was readily soluble in water. Subsequently it has been frequently reported that the formation of the carbon suboxide polymer as a side-product accompanies all prolonged reactions of carbon suboxide, particularly at an elevated temperature and in the presence of catalysts.

Special experiments have also been made on the polymerisation of carbon suboxide. It has been shown that pure carbon suboxide is fairly stable (does not polymerise at 0° over a period of several weeks [51]), whereas the insufficiently purified compound polymerises over a period of only several hours. The effect of various catalysts on the rate of polymerisation has been studied. Organic bases (pyridine, triethylamine, quaternary ammonium bases), sulphuric acid, aluminium chloride, boron trifluoride [51,52], and phosphorus pentoxide [1,66] have been tested. When catalysts are added to liquid carbon suboxide, the polymerisation takes place vigorously, often with explosion; in a solvent the reaction takes place smoothly and gradually. Pyridine and triethylamine proved to be the best catalysts [51]. The polymer is also obtained in good yield (80%) when solutions of carbon suboxide in halogen-containing solvents are γ-irradiated [133].

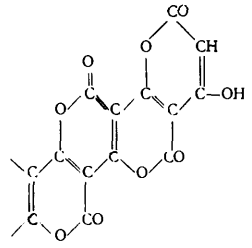
The problem of the structure of the carbon suboxide polymer has been the subject of lively discussion from the

moment of its discovery until the present time. Diels suggested that the red carbon suboxide polymer has a polycyclobutanedione structure[68]:



(I)

Later investigations of Schmidt and coworkers established that the polymer molecule includes also five- and six-membered lactone rings[134]. Ziegler suggested a poly-α-pyrone structure for the polymer[135]:



(II)

On the basis of the study of the infrared spectra of the polymer and its methyl ether, Hegar[51] rejects both structures (I) and (II), noting also that none of the polymers obtained had the composition $[C_3O_2]_x$. However, Blake and coworkers[136-138], who investigated the structure of the carbon suboxide polymer, again proposed a structure analogous to structure (II).

In the examination of the structures proposed one must bear in mind that the above investigators were scarcely likely to deal with identical compounds, since the conditions used in the preparation of the polymer were not the same. While Diels[1,68] and Hegar[51] obtained the carbon suboxide polymer at 0°C in the presence of chemical catalysts, Blake and coworkers[136] and other investigators[115] carried out the polymerisation at temperatures of the order of 100°C. Probably this is why the properties of the carbon suboxide polymers are so different[48]. It is also possible that the investigators dealt with structures analogous to both structure (I) and structure (II). Nor can one exclude the possibility of the formation of mixed structures, which may occur, for example, on further addition of carbon suboxide to the products of its interaction with enols; in this reaction two structures have been found to form, as in polymerisation — one with a carboxy-group analogous to structure (I)[51] and one with a polypyrone group, analogous to structure (II).[88]

In conclusion it should be noted yet again that further development of the chemistry of carbon suboxide is extremely promising both from the theoretical and practical points of view.

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SYNTHESIS AND SOME PROPERTIES OF αω-DISUBSTITUTED (DIFUNCTIONAL) POLYENES

L. A. Yanovskaya

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I. INTRODUCTION

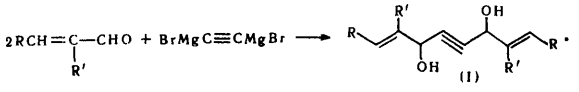
αω-Disubstituted (difunctional) polyenes are fairly widely distributed in nature. They include, for example, various branched and unbranched dicarboxylic acids (crocetin, bixin, corticrocin, descrocetin), which are the normal metabolites of certain plants and micro-organisms, polyene diketones (capsorubin – one of the pigments of cayenne, etc.). Many disubstituted difunctional polyenes are the degradation products of polyene antibiotics, such as, for example, fumagillin, lagosin, tetrin, etc. Finally, difunctional polyenes serve as the starting materials in the synthesis of other important natural compounds, for example, carotenoids (β-carotene, lycopene, etc.). In this connection synthetic methods have been investigated and developed for individual representatives of substances of this type, in the first place those with the isoprenoid structure; some of these have been described in reviews devoted to advances in the synthesis of carotenoids and vitamin A [1-3]. However, a complete description of the synthetic methods for αω-disubstituted (difunctional) polyenes has not been given so far. And yet in recent years considerable new advances have been achieved in this field, as a result of which the principal types of difunctional polyenes have become fully available. The advances in the synthetic field led to a number of theoretical findings based on the study of many properties of these compounds, particularly studies concerning the effect of the terminal substituents in the polyene chain on one another.

The present review is devoted to the advances in the synthesis of αω-disubstituted (difunctional) polyenes and certain properties of polyenes.

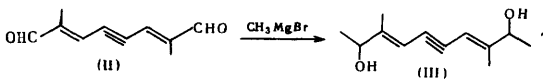
II. SYNTHESIS OF POLYENES WITH THE SAME SUBSTITUENTS AT THE ENDS OF THE CHAIN

Glycols

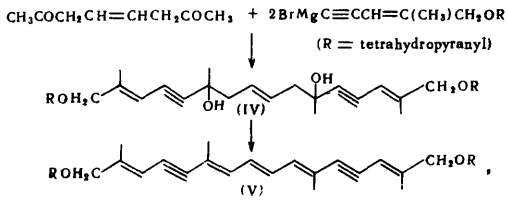
Primary and secondary glycols of the polyene and polyenyne series might serve as convenient starting compounds for the synthesis of other disubstituted (difunctional) polyenes, and therefore much attention has been devoted to their synthesis. The first and oldest method of preparing glycols consists in organometallic synthesis. This procedure leads mainly to secondary glycols. Best results have been obtained in the reaction of the simplest αβ-unsaturated monoaldehydes with the Iotsich complex. Thus when acrolein[4], methacrolein[5-11] or tiglic aldehydes[12] are allowed to act on bis(bromomagnesium)acetylene in ether, octa-1,7-dien-4-yne-3,6-diol (I, R = R′ = H), 2,7-dimethylocta-1,7-dien-4-yne-3,6-diol (I, R = H, R′ = CH_3), and 3,8-dimethyldeca-2,8-dien-5-yne-4,7-diol (I, R = R′ = CH_3) were obtained in yields of the order of 70%:



Dialdehydes and Grignard reagents can also be used in this reaction[12,13]. For example, the reaction of methylmagnesium bromide with 2,7-dimethylocta-2,6-dien-4-yne-1,8-dial (II) gave 3,8-dimethyldeca-3,7-dien-5-yne-1,9-diol (III):



However, attempts to synthesise primary glycols using the reaction between a Grignard reagent with the appropriate functional group and a diketone[14],



were not very successful because dehydration of compound (IV) gave the bistetrahydropyranyl ether (V) in a yield of only 8%.

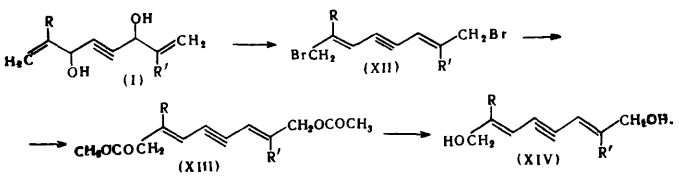
The attempt to use for the synthesis of glycols the Grignard reaction between hex-4-en-1-yn-3-ol (VI) or hex-3-en-1-yn-5-ol (VII) and acetaldehyde was also unsuccessful. Although the corresponding reaction products, oct-6-en-3-yne-2,5-diol (VIII) and oct-5-en-3-yne-2,7-diol (IX) are formed in high yields[15], selective hydrogenation of the glycol (IX) by chemical or catalytic methods gave octa-3,5-diene-2,7-diol (X) in a very low yield. The hydrogenation

of the glycol (VIII) took place smoothly, but the anionotropic rearrangement of the glycol (XI) gave mainly octa--4,6-diene-2,3-diol instead of the desired glycol (X):

$$\begin{array}{lll} CH_3CH{=}CHCH(OH)C{\equiv}CH & \rightarrow & CH_3CH(OH)CH{=}CHC{\equiv}CH \\ (VI) \quad \downarrow & & (VII) \quad \downarrow \\ CH_3CH{=}CHCH(OH)C{\equiv}CCH(OH)CH_3 & \rightarrow & CH_3CH(OH)CH{=}CHC{\equiv}CCH(OH)CH_3 \\ (VIII) \quad \downarrow & & (IX) \quad \downarrow \\ CH_3CH{=}CHCH(OH)CH{=}CHCH(OH)CH_3 & & CH_3CH(OH)(CH{=}CH)_2CH(OH)CH_3. \\ (XI) & & (X) \end{array}$$

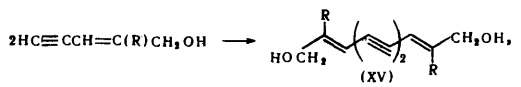
Thus organometallic synthesis can be used conveniently only for the synthesis of the simplest secondary glycols, based on monoaldehydes and the Iotsich reagent.

Anionotropic rearrangement is used for the preparation of primary glycols[5,7-9], but this frequently does not take place smoothly. Comparatively recently a new method has been proposed for the conversion of secondary glycols into primary glycols[11], in which the secondary glycol (I) is converted into the primary dibromide (XII) by the action of phosphorus tribromide[10] or hydrobromic acid[6,11]; the dibromide (XII) is then converted into the diacetate (XIII) by treatment with sodium acetate and the product (XIII) is hydrolysed with alkali to give the primary glycol (XIV). All the conversions take place readily and the yield of the glycol (XIV) is fairly high:



It should be noted incidentally that this promising method for the conversion of secondary glycols into primary glycols has so far been developed only for a few isolated cases.

A second synthetic method, which is suitable for the preparation of both primary and secondary glycols, is based on the oxidative coupling of primary or secondary enyne alcohols. Thus the corresponding primary enyne glycols (XV) were obtained in a high yield from pent-2-en--4-yn-1-ol or 2-methylpent-2-en-4-yn-1-ol[14]:



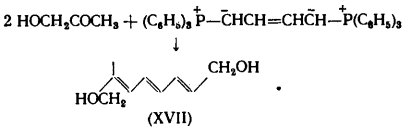
where R = H or CH_3.

The oxidative coupling reaction is used particularly extensively for the synthesis of secondary glycols[15-18]. For example, the oxidative coupling of the readily available but-3-yn-2-ol[17,18] gave the diacetylene glycol (XVI), the reduction of which led to the glycol (X):

$$HC{\equiv}CCH(OH)CH_3 \rightarrow HOCH(CH_3)(C{\equiv}C)_2CH(CH_3)OH \rightarrow (X).$$
(XVI)

Despite the ready availability of the initial enyne alcohols and the high yields of the glycols, this method has one important disadvantage: the selective reduction of the diacetylene system often constitutes a very difficult problem. Therefore, despite the obvious advantages of this method for the synthesis of glycols, preference is given at the present time to organometallic synthesis.

Quite recently yet another synthetic procedure for primary polyglycols has been described[19] — the Wittig reaction between 2-butene-1,4-diylidenebis(triphenylphosphorane) and hydroxyacetone, but the yield of the product (XVII) was only 10%:

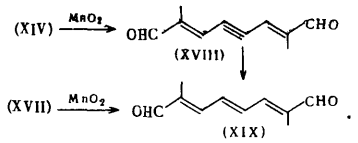


Dialdehydes

Dialdehydes are the most important starting compounds for reactions whereby substances of other classes can be obtained. Only the successful discovery of readily accessible and simple methods for the synthesis of dialdehydes of the polyene and polyenyne series could lead to the ready availability of the principal types of difunctional polyenes. In this connection, the interest shown by many investigators in this problem is fully justified.

The first synthetic procedure for dialdehydes was based on the oxidation of primary polyene glycols or polyenyne glycols with subsequent selective hydrogenation of the triple bonds. Each of the modifications proposed differed from the others by the method of synthesising the initial glycols (see above).

The oxidation of glycols of type (XIV) or (XVII) by the Oppenauer method or with t-butyl chromate is unsuccessful. Excellent results are, however, obtained in the presence of activated manganese dioxide[6-10], the yields of dialdehydes of type (XVIII) or (XIX) reaching 85–95%:

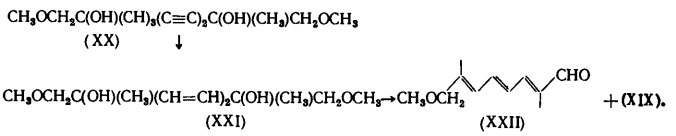


However, this universal method is not very suitable for the preparation of large amounts of dialdehydes because of the necessity to use extremely large amounts of manganese dioxide and solvent. Furthermore, the scope of this method is also restricted by the low availability of the starting compounds, because, as pointed out above, only the simplest glycols can be regarded as readily available.

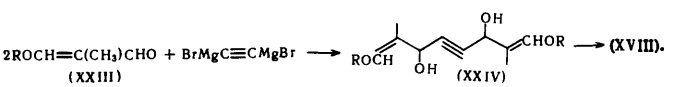
The hydrogenation of enyne dialdehydes to polyene dialdehydes takes place best in the presence of Lindlar's catalyst[7,20]. The *cis*-isomers produced in this process are isomerised to the *trans*-form on standing, on boiling in benzene solution, or under the action of traces of iodine or ultraviolet light.

The second method which was developed to prepare polyene dialdehydes consists in the synthesis of divinyl ethers, which are then hydrolysed to the dialdehydes. For example, oxidative dimerisation of 1-methoxy-2-methylbut-3-yn-2--ol[21,22] gives 1,8-dimethoxy-2,7-dimethylocta-3,5-diyne--2,7-diol (XX), the reduction of which with lithium aluminium hydride leads to the *trans-trans*-dienediol (*trans*-XXI), while hydrogenation in the presence of palladium poisoned with quinoline leads to the *cis-cis*-dienediol (*cis*-XXI).

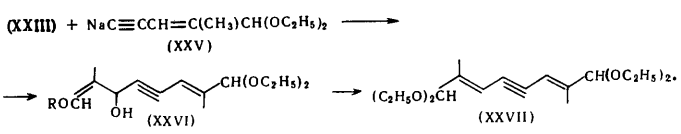
However, dehydration and hydrolysis of both dienediols resulted in a mixture of the dialdehyde (XIX) and the monoaldehyde (XXII):



It has also been suggested that the aldovinyl ether (XXIII) be condensed with the Iositch complex[23,24] and that the resulting divinyl ether (XXIV) be hydrolysed to the dialdehyde (XVIII):

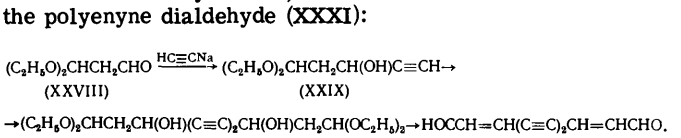


In another modification of this method[23,24] the aldovinyl ether (XXIII) is condensed with the sodio-derivative of the diethyl acetal of 2-methylpent-2-en-4-ynal (XXV) to give the hydroxy-acetal (XXVI), the latter being hydrolysed with the formation of the bisacetal (XXVII) without isolating in a pure form the intermediate dialdehyde (XVIII):

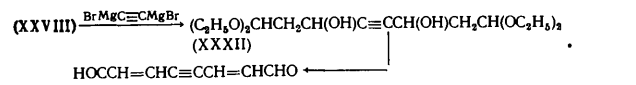


The method described above gives satisfactory yields of the final products, but it is not general.

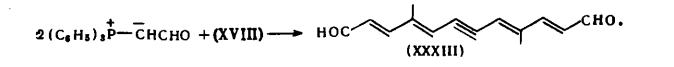
The third method for the synthesis of dialdehydes is also non-general. In this procedure $\beta\beta$-diethoxypropionaldehyde (XXVIII) is condensed with sodium acetylide or the Iositch reagent[25]. The hydroxy-acetal (XXIX) obtained in the first case is subjected to oxidative dimerisation to the dihydroxy-bisacetal (XXX) and the latter is hydrolysed with simultaneous dehydration, which leads to the formation of the polyenyne dialdehyde (XXXI):



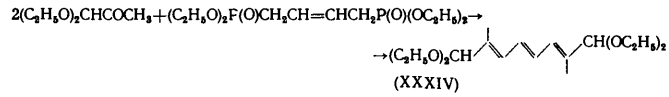
In the second case the resulting dihydroxy-bisacetal (XXXII) is also hydrolysed with simultaneous dehydration:



The fourth method for the synthesis of dialdehydes is based on the Wittig reaction. It was found[26] that formylmethylenetriphenylphosphorane reacts with the dialdehyde (XVIII), the product being 4,9-dimethyldodeca-2,4,8,10-tetraen-6-yne-1,12-dial (XXXIII):

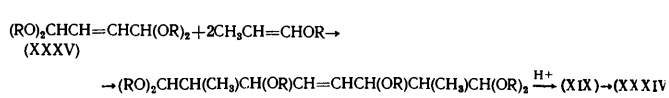


However, despite the fact that according to spectroscopic data the yield of compounds (XXXIII) was 50%, the amount of the dialdehyde isolated from the reaction mixture was only 15%, this being due, according to the authors, to the difficulty of separating compound (XXXIII) from triphenylphosphine oxide. Incidentally, the attempt[27] to increase the yield of compound (XXXIII) by using in the reaction with the dialdehyde (XVIII) formylmethylene(*p*-diethylaminophenyl)diphenylphosphorane, the oxide formed from which is readily soluble in dilute hydrochloric acid, was unsuccessful: the yield of the dialdehyde (XXXIII) was only 12%. A patent[19] describes the synthesis of the bis(diethyl acetal) of 2,7-dimethylocta-2,4,6-triene-1,8-dial (XXXIV) in the reaction between the diphosphonate (obtained from 1,4-dichlorobutene and triethyl phosphite) and the acetal of methylglyoxal:



However, these data have not been confirmed so far. Furthermore, the method described is to some extent non-general.

Until recently, despite the many attempts made, there was no simple general and reliable method for the synthesis of polyene dialdehydes, based on readily available starting materials. Such a method was developed on the basis of the reaction of divinyl ethers with acetals of aldehydes. It involves three stages: (1) the conversion of the dialdehyde into the bisacetal, (2) the condensation of the bisacetal with two moles of vinyl ether [catalysts $BF_3(C_2H_5)_2O$, $ZnCl_2$, etc.], and finally (3) hydrolysis of the resulting dialkoxy-bisacetal with simultaneous removal of the alkoxy-groups by heating with a solution of sodium acetate in acetic acid, or with phosphoric acid, etc. Usually all three stages are carried out in succession without isolating and purifying the products and thus they are in fact combined into a single stage. This method was first used for the synthesis of isoprenoid dialdehydes[28-36] from the bisacetal of but-2-ene-1,4-dial (XXXV):



The dialdehyde (XIX), which is a key product of fundamental importance, was obtained in this way. The repetition of this procedure with the bisacetal (XXXIV) using ethyl vinyl ether gave 4,9-dimethyldodeca-2,4,6,8,10-pentaenedial and subsequently crocetin dialdehyde. This synthetic procedure was proposed[37-39] for the preparation of unbranched dialdehydes of the type $OHC(CH{=}CH)_nCHO$. It is noteworthy that all the stages of the synthesis often take place with very high yields and lead to the formation of pure products.

Since bisacetals of but-2-ene-1,4-dial are nowadays readily available[37-38], the above method may be regarded as ideal for the synthesis of polyene dialdehydes. Here we have a harmonious combination of ready availability of the starting materials and the ease of the synthetic procedure and the isolation and purification of the product, which makes this method superior to all others. The method is also flexible and universal. Thus polyene dialdehydes have now become fully available.

It is noteworthy that both maleic and fumaric bisacetals react with ethyl vinyl ether equally readily[37-39], the condensation of maleic bisacetal (increase in size) being

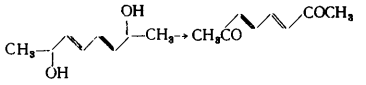
accompanied by a complete conversion of the *cis*-configuration into the *trans*-configuration[37]. In contrast to this, the condensation of the bisacetal of *cis-cis*-muconic dialdehyde[25] is not accompanied by complete isomerisation and leads to a mixture of isomeric dialkoxy-bisacetals. However, hydrolysis of the dialkoxy-bisacetals results, as a rule, in the formation of only the pure *trans*-isomers.

Asymmetric condensation (increase in the chain length) of the bis(dimethyl acetal) of fumaric dialdehyde using ethyl vinyl ether and butyl vinyl ether was achieved by Makin[39], but the yields of products were only 16–20%:

$$(CH_3O)_2CHCH{=}CHCH(OCH_3)_2+CH_2{=}CHOCH_3\rightarrow$$
$$\rightarrow(CH_3O)_2CHCH{=}CHCH(OCH_3)CH_2CH(OCH_3)_2.$$

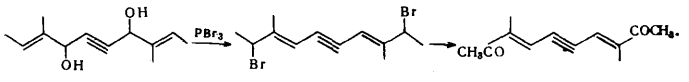
Diketones

Three procedures have been proposed for the synthesis of polyene diketones. The first is based on the oxidation of secondary glycols, using activated manganese dioxide[15]. For example, the oxidation of the secondary glycol (XXXVI) gives the diketone (XXXVII) in 91% yield (when aluminium t-butoxide was used, the yield fell to 5%):



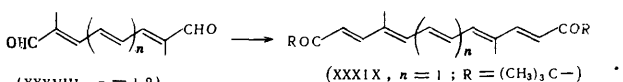
(XXXVI) (XXXVII)

Secondary glycols are also converted into diketones by a reaction involving the initial conversion into bromides (with isomerisation), this being followed by oxidation with 2-nitropropane in an alkaline medium[11]:



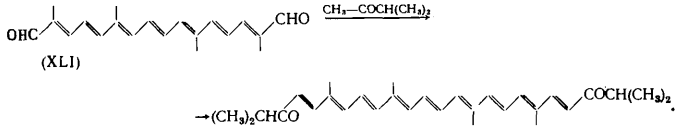
The oxidative method for the synthesis of diketones suffers from the same disadvantages as the oxidative method for the synthesis of dialdehydes (see above) and its scope is also restricted by the availability of the initial glycols.

The second method for the synthesis of polyene diketones is based on the Claisen condensation[40-43] in the presence of aluminium t-butoxide[14,41,42], an alcoholic solution of potassium hydroxide[43], and piperidine or piperidinium acetate[44-47]. In most cases this procedure leads to fairly high yields of diketones. Thus the condensation of 2,7-dimethylocta-2,4,6-triene-1,8-dial (XXXVIII, n = 1) with pinacoline in the presence of aluminium t-butoxide gives the diketone (XXXIV, n = 1) in 35% yield. Under the same conditions hexaene diketones (XI, n = 2) were obtained in yields of 40–50% from the dialdehyde (XXXVIII, n = 2) and acetone or pinacoline[41,42]:



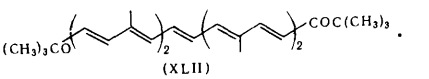
(XXXVIII, n = 1,2) (XXXIX, n = 1; R = $(CH_3)_3C-$)
(XL, n = 2; R = CH_3, $(CH_3)_3C-$)

The condensation of isopropyl methyl ketone with crocetin dialdehyde (XLI) in the presence of alcoholic potassium hydroxide at room temperature also takes place with high yields (70–80%)[43]:



(XLI)

However, the condensation of the dialdehyde (XXXVIII, n = 1) with tiglylidenepinacolone gave the diketone (XLII) in a yield of only 1–2%:[42]



(XLII)

The Claisen condensation was also used in the synthesis of the natural polyene diketone canthaxanthin[42], the results also being satisfactory.

Since at the present time polyene dialdehydes are readily available, the above method for the synthesis of polyene diketones is undoubtedly convenient and simple.

Finally the third method for the synthesis of polyene diketones consists in the Wittig reaction between acylmethylenetriphenylphosphoranes and polyene dialdehydes[48]:

$$OHC(CH{=}CH)_nCHO+2(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOR\rightarrow RCO(CH{=}CH)_{n+2}COR$$

(XLIII) n=2, 3, 4; R=CH_3, C_6H_5
n=2, 3, 4

The reaction takes place readily on heating acetylmethylenetriphenylphosphorane or benzoylmethylenetriphenylphosphorane with dialdehydes (XLIII) in benzene or toluene. The yields of polyene diketones reach 60–68%. The polyenes thus obtained are entirely in the *trans*-configuration. When the initial aldehydes are available, both the Wittig reaction and the Claisen condensation can be successfully used for the synthesis of polyene diketones.

We may conclude that at the present time polyene diketones are also fully accessible.

Dicarboxylic Acids and Their Esters

A number of synthetic procedures have been proposed for polyenedicarboxylic acids. The first, oldest method is based on the condensation of monocarboxylic acid esters with diethyl oxalate in the presence of alkaline reagents[49-51]:

$$C_2H_5OOCCOOC_2H_5+CH_3(CH{=}CH)_mCOOC_2H_5\rightarrow C_2H_5OOCCOCH_2(CH{=}CH)_mCOOC_2H_5\rightarrow$$
(XLIV) (XLV)
$$\rightarrow C_2H_5OOCC(OCOCH_3){=}CH(CH{=}CH)_mCOOC_2H_5\rightarrow$$
(XLVI)
$$\rightarrow C_2H_5OOCCH(OCOCH_3)(CH{=}CH)_mCH_2COOC_2H_5\rightarrow HOOC(CH{=}CH)_nCOOH$$
(XLVII) (XLVIII)

The condensation of the polyene ester (XLIV) with diethyl oxalate into the keto-diester (XLV) takes place in yields of 65–70% with the lower members of the series (XLIV, n = 1, 2), but with higher members (n = 4–6) the yields fall to 10–27%. The acetylation of the keto-diester (XLV) with acetic anhydride to give the compound (XLVI) takes place smoothly as a rule, but the reduction of the compound (XLVI) with aluminium amalgam or zinc dust in a mixture of pyridine and acetic acid is sometimes not smooth, for example in the case of compound (XLVI, n = 6), and is accompanied by hydrogenolysis with formation of the diester of dihydrodescrocetin[51]. Finally treatment of the compound (XLVII) with a solution of alkali gives the polyenedicarboxylic acid (XLVIII) containing one double bond more than the initial monocarboxylic acid ester (XLIV). The dicarboxylic acids (XLVIII, n = 3, 4, 5, 7) were obtained by this method. The main disadvantage of the method is the large number of stages. Furthermore, the method is not general — the attempts to extend it to the synthesis of branched higher polyene acids (crocetin, bixin) were unsuccessful.

The second method for the synthesis of polyenedicarboxylic acids consists in the oxidative dimerisation of acetylenemonocarboxylic acids with subsequent alkaline isomerisation of the resulting diacetylenedicarboxylic acids into polyenedicarboxylic acids[52,53]. The first complete synthesis of corticrocin (XLVIII, $n = 6$) was achieved by this method. For this purpose, the diacetylenedicarboxylic acid (L) was obtained by the oxidative coupling of hept-2-en-6-ynoic acid (XLIX), the salt of corticrocin being obtained by boiling the acid (L) with an aqueous solution of potassium hydroxide:

$$\underset{\text{(XLIX)}}{HC{\equiv}CCH_2CH_2CH{=}CHCOOH} \rightarrow \underset{\text{(L)}}{HOOCCH{=}CHCH_2CH_2(C{\equiv}C)_2CH_2CH_2CH{=}CHCOOH} \rightarrow \rightarrow \text{(XLVIII, } n = 6)$$

This comparatively simple procedure gives, however, very low yields of the final product, mainly due to the stage involving the isomerisation of diacetylene. Furthermore, the initial polyenynoic acids are also usually not readily accessible.

A more convenient modification is the direct dimerisation of the enynoic acids or their esters with subsequent selective hydrogenation of the resulting acetylenedicarboxylic acids or their esters[14,25]. For example:

$$HC{\equiv}C(CH{=}CH)_nCOOC_2H_5 \rightarrow \underset{\text{(LI)}}{C_2H_5OOC(CH{=}CH)_n(C{\equiv}C)_2(CH{=}CH)_nCOOC_2H_5} \rightarrow$$

$$\rightarrow \underset{\text{(LII)}}{C_2H_5OOC(CH{=}CH)_n(CH{=}CH)_{\overset{cis}{2}}(CH{=}CH)_nCOOC_2H_5} \rightarrow \underset{\text{(LIII)}}{C_2H_5OOC(CH{=}CH_2)_{n+2}COOC_2H_5}.$$

Polyenedicarboxylic acids with central *cis*-bonds can be obtained by this procedure. The diethyl esters of 4,6-*cis*-*cis*-deca-2,4,6,8-tetraene-1,10-dioic acid (LIII, $n = 1$) and 6,8-*cis*-*cis*-corticrocin (LIII, $n = 2$) were obtained in this way.

It is noteworthy that on hydrogenation of compound (LI, $n = 2$) in the dark at a weight ratio substance : catalyst = = 0.5, the *cis*-*cis*-isomer (LII, $n = 2$) forms, while at a weight ratio substance : catalyst = 1.5 the product is the diethyl ester of *cis*-*cis*-corticrocin, which is also produced by the isomerisation of (LII, $n = 2$).[25] The use of this modification leads to high yields of the final products, but its application is restricted by the availability of the initial enyne esters.

Yet another modification of the synthetic procedure has been proposed for the preparation of polyenedicarboxylic acids[54]. Thus dimersiation of pent-2-en-4-ynol yields the primary glycol (LIV), which is converted into the dibromide (LV) under the action of phosphorus tribromide. On treatment under copper cyanide, the latter yields the dinitrile (LVI). Hydrolysis of compound (LVI) with a solution of hydrogen chloride in methanol yields the dimethyl ester (LVII), which is converted by alkaline isomerisation into the dimethyl ester of dodeca-2,4,8,10-tetraen-6-yne-1,2-dionic acid (LVIII). When the compound (LVIII) is hydrogenated in the presence of Lindlar's catalyst and isomerised, the dimethyl ester of dodeca-2,4,6,8,10-pentaenedioic acid (LIX), fully in the *trans*-configuration, is obtained:

$$\rightarrow \underset{\text{(LVI)}}{NCCH_2CH{=}CH(C{\equiv}C)_2CH{=}CHCH_2CN} \rightarrow \underset{\text{(LVII)}}{CH_3OOCCH_2CH{=}CH(C{\equiv}C)_2CH{=}CHCH_2COOCH_3} \rightarrow$$

$$\rightarrow \underset{\text{(LVIII)}}{CH_3OOC(CH{=}CH)_2C{\equiv}C(CH{=}CH)_2COOCH_3} \rightarrow \underset{\text{(LIX)}}{CH_3OOC(CH{=}CH)_6CO}.$$

All the stages of the synthesis take place with fairly high yields, but, as a whole, the synthesis is inconvenient in view of the large number of stages and the limited availability of the initial compound.

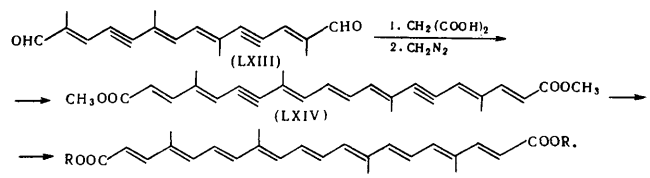
In a procedure similar to that described above[54] the ester of the tetracarboxylic acid (LX), obtained by the reaction of the dibromide (LV) with the potassiomalonic ester, is hydrolysed and decarboxylated to the dicarboxylic acid (LXI) and the latter is isomerised to give corticrocin (XLVIII, $n = 6$). This modification suffers from the disadvantage characteristic of the synthesis involving the dinitrile formation stage (see above) and in addition it is inconvenient because in the last two stages the yields of products are low:

$$\text{(LV)} + KHC(COOC_4H_9\text{-}t)_2 \rightarrow$$

$$\rightarrow \underset{\text{(LX)}}{(t\text{-}C_4H_9OOC)_2CHCH_2CH{=}CH(C{\equiv}C)_2CH{=}CHCH_2CH(COOC_4H_9\text{-}t)_2} \rightarrow$$

$$\rightarrow \underset{\text{(LXI)}}{HOOCCH_2CH_2CH{=}CH(C{\equiv}C)_2CH{=}CHCH_2CH_2COOH} \rightarrow \text{(XLVIII, } n = 6).$$

The third method of synthesising polyenecarboxylic acids is based on the Doebner reaction applied to polyene and polyenyne dialdehydes[14,41,42,54]. The first complete synthesis of bixin (LXII) was achieved in this way[14]:

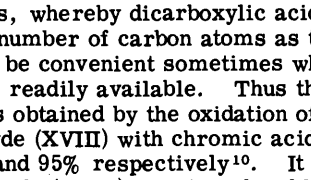


For this purpose, the enyne dialdehyde (LXIII) is condensed with malonic acid by heating in pyridine in the presence of piperidine, the resulting acid is esterified with diazomethane, the dimethyl ester of 6,7,14,15-bisdehydrobixin (LXIV) being obtained in 20% yield (in two stages); its hydrogenation in the presence of Lindlar's catalyst gave the dimethyl ester of *trans*-bixin (LXII), probably via the intermediate *cis*-forms.

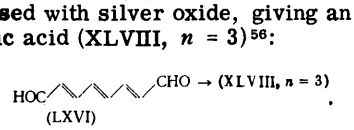
2,2'-bisnorcrocetin was obtained similarly by the condensation of 2,7-dimethylocta-2,4,6-triene-1,8-dial with ethylidenemalonic acid in the presence of trimethylbenzylamine oxide at room temperature[41]. However, attempts to condense 2,9-dimethyldeca-2,8-diene-4,6-diyne-1,10-dial with malonic acid were unsuccessful[54].

The Doebner reaction can probably be sometimes successfully employed in the synthesis of polyenedicarboxylic acids, because at the present time the corresponding dialdehydes are readily available.

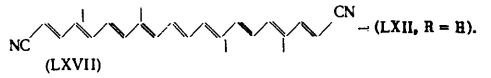
The fourth synthetic procedure for polyenedicarboxylic acids consists in the oxidation of the corresponding glycols and dialdehydes, whereby dicarboxylic acids are obtained with the same number of carbon atoms as the initial compound. It can be convenient sometimes when the initial compounds are readily available. Thus the dicarboxylic acid (LXV) was obtained by the oxidation of the glycol (XIV) or the dialdehyde (XVIII) with chromic acid mixture in yields of 30% and 95% respectively[10]. It is interesting that the dialdehyde (XVIII) is not oxidised by silver oxide:



On the other hand, octa-2,4,6-triene-1,8-dial (LXVI) is smoothly oxidised with silver oxide, giving an 88% yield of the dicarboxylic acid (XLVIII, $n = 3$)[56]:

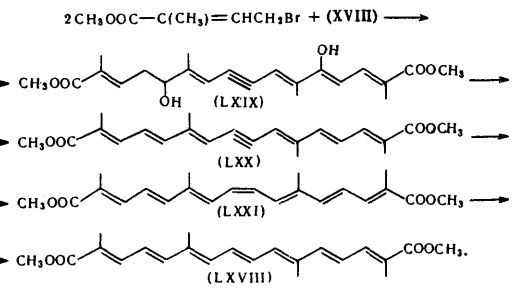


The fifth method of synthesis of polyenedicarboxylic acids consists in the hydrolysis of dinitriles. It also yields polyenedicarboxylic acids with the same number of carbon atoms and can find limited application when the dinitriles are available. Thus norbixin (LXII, R = H), with a fully *trans*-configuration, was obtained on cautious hydrolysis of the dinitrile (LXVII)[55]:



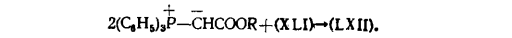
→ (LXII, R = H).

The sixth method is based on the Reformatsky reaction between polyene and polyenyne dialdehydes and bromo--acid esters. The syntheses of the dimethyl ester of crocetin (LXVIII) and methyl bixin (LXII) were achieved in this way[7,8,13]. For example, the acetylenic dialdehyde (XVIII) is made to undergo the Reformatsky reaction with methyl γ-bromotiglate in tetrahydrofuran under carefully selected conditions, the glycol (LXIX) being obtained in high yield. Dehydration of the glycol (LXIX) with *p*-toluenesulphonic acid gives the dimethyl ester of 8,8′-dehydrocrocetin (LXX). On hydrogenating the compound (LXX) and then isomerising the dimethyl ester of 8,8′-*cis*--crocetin (LXXI) by irradiation with ultraviolet light in the presence of iodine, the dimethyl crocetin ester (LXVIII), fully in the *trans*-configuration, is obtained:

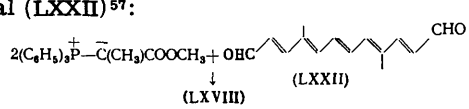


A bottleneck in the application of the Reformatsky reaction to the synthesis of polyenedicarboxylic acids is the stage involving the dehydration of the resulting hydroxy--esters, in which the yields are frequently very low [for example, the dehydration of compound (LXIX) gave compound (LXX) in a yield of only 1%].

The seventh method of synthesis of polyene dicarboxylic acids is based on the Wittig reaction between polyene or polyenyne dialdehydes and alkoxycarbonylmethylenediphenylphosphoranes or the diethyl esters of alkoxycarbonylmethylphosphonic acids, or their derivatives. Isler[57] was the first to apply the Wittig reaction in the synthesis of isoprenoidpolyenedicarboxylic acids. Thus a number of norbixin esters (LXII) were obtained in high yields (75–85%) on boiling a benzene solution of crocetin dialdehyde (XLI) with alkoxycarbonylmethylenetriphenylphosphoranes:

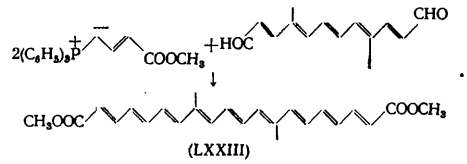


The use of α-alkoxycarbonylethylidenetriphenylphosphoranes permits the introduction not only of the alkoxycarbonylmethylene group but also of a methyl side-group. The dimethyl ester of crocetin (LXVIII) was thus obtained in 80–95% yield from α-methoxycarbonylethylidenetriphenylphosphorane and 4,9-dimethyldodeca-2,4,6,8,10-pentaene--1,12-dial (LXXII)[57]:



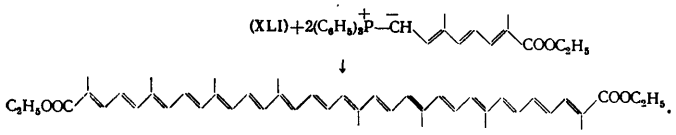
The esters of 8,8′-dehydrocrocetin and 10,10′-dehydronorbixin were obtained similarly[58].

Phosphoranes obtained from unsaturated ω-halogeno--acids can also be used in the synthesis of polyenedicarboxylic acids. For example, it has been proposed that the dimethyl ester of crocetin (LXVIII), the dimethyl ester of norbixin (LXII, R = CH_3), and dimethyl ester of 4,4′-desmethylnorbixin (LXXIII) be synthesised by the condensation of the corresponding dialdehydes with phosphoranes obtained from the methyl esters of γ-bromodimethylacrylic, γ-bromocrotonic, and γ-bromotiglic acids[59–62]:

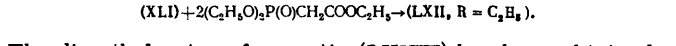


The yields of the final products reach 75–80%.

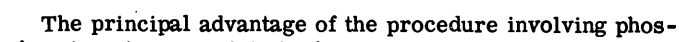
However, the use of the phosphoranes derived from the methyl ester of 4-methyl-6-bromosorbic acid and the ethyl ester of 2,6-dimethyl-8-bromo-octa-2,4,6-trienoic acid[63] results in much lower yields of the final product (of the order of 15%). For example,



A convenient modification of the Wittig reaction has been described in patents[19,64], where it is suggested that phosphonates be used instead of phosphoranes. Thus a solution of the diethyl ester of an ethoxycarbonylmethylphosphonic acid in dimethylformamide is treated with sodium alkoxide and then crocetin dialdehyde (XLI) is introduced into the reaction mixture, which leads to a high yield of the diethyl ester of norbixin (LXII, R = C_2H_5):

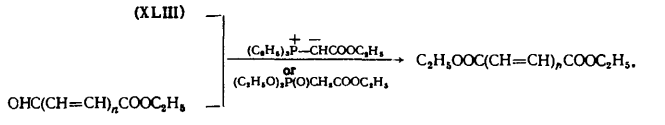


The dimethyl ester of crocetin (LXVIII) has been obtained similarly from the dialdehyde (XIX) and diethyl (3-methoxycarbonylbut-2-en-1-yl)phosphonate:



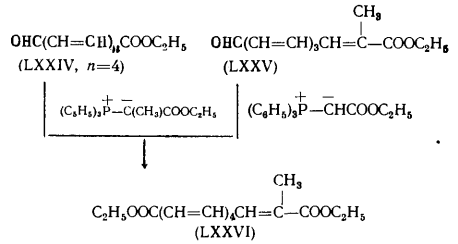
The principal advantage of the procedure involving phosphonate esters consists in the exceptional ease with which the final products are isolated, frequently by simple dilution of the reaction mixture with water, while the compounds formed in the presence of phosphoranes are often difficult to purify from triphenylphosphine oxide.

Both modifications of the Wittig reaction have been used for the synthesis of unbranched polyene acids[25,37,65,66]:



For example the diethyl esters of descrocetin and corticrocin have been synthesised in this way.

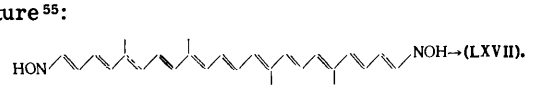
In the reaction of ethoxycarbonylvinylmethylenetriphenylphosphorane with unbranched dialdehydes the yields of the final products are only 9–13%, which is much lower than in the reaction where unbranched isoprenoid dialdehydes or ethoxycarbonylmethylenetriphenylphosphorane are used. However, this is frequently compensated by the fact that more readily available lower polyene dialdehydes serve as the starting materials in the reaction. The use of esters of aldehydo-acids (LXXIV) permits the synthesis of esters of asymmetric dicarboxylic acids[65]. The diethyl ester of 2-methyldodeca-2,4,6,8,10-pentaene-1,12-dioic acid (LXXVI), a degradation product of natural fungichromin, was obtained by the reaction of the aldehyde (LXXIV, n = 4) with α-ethoxycarbonylethylidenetriphenylphosphorane or the aldehyde (LXXV) with ethoxycarbonylmethylenetriphenylphosphorane:



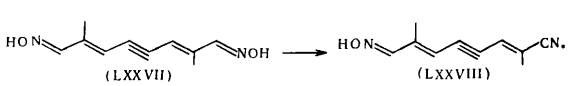
The study of the stereochemistry of the Wittig reaction with unbranched aldehydes and esters of aldehydo-acids[38,65,66] showed that in all cases the reaction is stereospecific, the *trans*-isomers of the polyenedicarboxylic acid esters being formed exclusively. On the basis of the analysis of the above data, one may conclude that the synthesis based on the use of phosphonates is the most convenient because of the ease with which it can be carried out, the ease of isolating the final products, and because of the high yields of the diesters. The application of this synthesis in practice made a wide variety of polyenedicarboxylic acid esters of different structures readily available.

Dinitriles

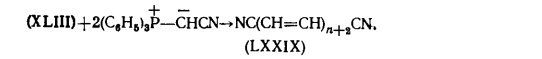
Comparatively recently the dinitriles of polyenedicarboxylic acids were almost unknown. Only the dinitrile of bixin (LXVII), obtained by the dehydration of bixin dialdehyde dioxime with acetic anhydride, was described in the literature[55]:



Recently the same procedure was used to prepare octa-2,4,6-triene-1,8-dinitrile[56] from the dioxime of octa-2,4,6-trienedial. However, this procedure cannot be regarded as sufficiently satisfactory, because the preparation and isolation of the dioximes of unsaturated aldehydes often constitute a very complex problem. Furthermore, the conversion of dioximes into dinitriles is not always possible. Thus dehydration of the dioxime (LXXVII) leads only to the hydroxyimino-nitrile (LXXVIII)[10]:



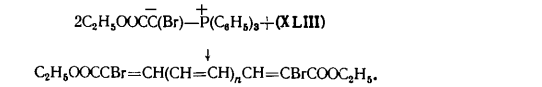
The second method of synthesising dinitriles, based on the Wittig reaction between cyanomethylenetriphenylphosphorane or diethyl cyanomethylphosphonate with polyene dialdehydes, is much more promising[25]. This procedure has been successfully applied in the preparation of a number of polyene-dinitriles (LXXIX):



As in the synthesis of the esters of polyenedicarboxylic acids, the employment of phosphonates greatly facilitates the isolation of the dinitriles from the reaction mixture and their purification. The yields of the dinitriles are quite satisfactory, reaching 50–70%. Thus polyene dinitriles too can now be regarded as fully accessible compounds.

Esters of $\alpha\alpha'$-Dibromopolyene Acids

Earlier these compounds were unknown. The possibility of their synthesis arose when the readily accessible synthetic procedure for dialdehydes had been developed and ethoxycarbonylbromomethylenetriphenylphosphorane began to be used in the Wittig reaction[25]:



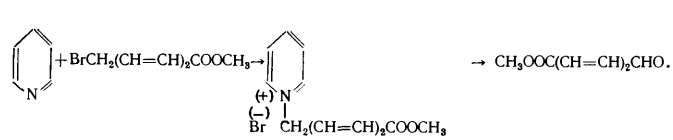
The yields of the final products range from 63 to 90%.

III. SYNTHESIS OF POLYENES WITH DIFFERENT SUBSTITUENTS AT THE ENDS OF THE CHAIN

Until recently polyenes with different substituents at the ends of the chain were relatively unknown and virtually no methods for their synthesis were developed. General methods for the synthesis of acetals of the type $(R'O)_2CH-R-Y$, where Y is a functional group and R a polyene chain, were found only in very recent years, which made it possible to develop general synthetic procedures for polyenes substituted in a wide variety of ways, based on the increase in the length of the polyene chain by condensation with vinyl ethers, with subsequent conversion of the aldehyde group into any other functional group by the Wittig reaction or other reactions. Thus polyene series with various substituents at the ends of the chain, which were formerly difficult to obtain or altogether unknown, became available.

Esters of Aldo-Acids and Their Acetals

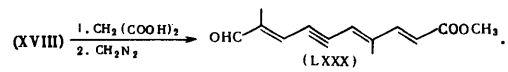
The synthesis of the lowest member of the series of polyene aldo-acids was achieved as follows[67]:



However, this method of synthesis was not extended to higher members of the series.

The ester of the aldo-acid (LXXX) was obtained in 10% yield by the Doebner condensation of the dialdehyde (XVIII)

with malonic acid and subsequent esterification with diazomethane:



New synthetic procedures for aldo-acid esters (LXXXI) became available when the reaction involving an increase in the chain length of the acetals of aldo-acids by condensation with vinyl ethers was proposed[65,68,69]:

$$(RO)_2CH(CH{=}CH)_nCOOC_2H_5 + CH_2{=}CHOC_2H_5 \rightarrow$$
$$\rightarrow (RO)_2CHCH_2CH(OC_2H_5)(CH{=}CH)_nCOOC_2H_5 \rightarrow OHC(CH{=}CH)_{n+1}COOC_2H_5.$$
(LXXXI; n=1–4)

A similar reaction was used to prepare the ethyl ester of 5-formyl-2-methylhexa-2,6-dienoic acid[68,69] and for the synthesis of asymmetrically substituted polyene aldo-acids[65]:

$$(RO)_2CH(CH{=}CH)_nCH{=}C(CH_3)COOC_2H_5 + CH_2{=}CHOC_2H_5 \rightarrow$$
$$\rightarrow (RO)_2CHCH_2CH(OR)(CH{=}CH)_nCH{=}C(CH_3)COOC_2H_5 \rightarrow OHC(CH{=}CH)_{n+1}CH{=}C(CH_3)-.$$
$$-COOC_2H_5 \quad (n=1-3)$$

These modifications of the synthesis were quite realistic and easy to carry out, because a simple method had been developed for the preparation of the initial acetals of aldo-acids by the Wittig reaction between readily available monoacetals of glyoxal and but-2-ene-1,4-dial (fumaric dialdehyde) and ethoxycarbonylmethylenetriphenylphosphorane (or better the diethyl ester of ethoxycarbonylmethylphosphonic acid)[65,70,71]:

$$(C_2H_5O)_2CH(CH{=}CH)_nCHO \rightarrow (C_2H_5O)_2CH(CH{=}CH)_nCH{=}C(R)COOC_2H_5.$$
(n=0, 1, 2) (n=0, 1, 2; R=H, CH_3)

Acetals of symmetrical and asymmetric aldo-acids were thus obtained in high (up to 70%) yields; these acids could also be hydrolysed to the corresponding aldehydes in the presence of phosphoric acid.

An unusual method for the synthesis of the ethyl ester of 10-formyldeca-2,4,6,8-tetraenoic acid (LXXXI, n = 3), based on the reaction of octa-2,4,6-triene-1,8-dial (XLIII, n = 3) with an equimolar amount of ethoxycarbonylmethylenetriphenylphosphorane in benzene solution, which involves preferentially one of the aldehyde groups, was proposed quite recently by Kovalev et al.[72] This method is particularly promising for the synthesis of higher asymmetrically substituted polyenes, because the dialdehyde (XLIII, n = 3) is very readily available, and the acetal can be smoothly obtained from the ester of the aldo-acid (XXXI, n = 3).

The development of a general method of synthesis of monoacetals of dialdehydes and esters of aldo-acids has opened up wide possibilities for the synthesis of other polyenes substituted with various functional groups.

Aldo-Nitriles and Their Acetals

The starting material for the synthesis of a number of polyene aldo-nitriles and their acetals has been the monoacetal of fumaric dialdehyde, the reaction of which with the diethyl ester of cyanomethylphosphonic acid gave a 70% yield (with cyanomethylenetriphenylphosphorane the yield was much lower) of the acetal of 5-cyanopenta-2,4-dien-1-al (LXXXII) as a mixture of *cis-trans*-isomers (in this case the Wittig reaction is not stereospecific)[25,73]. The increase in the chain length of the compound (LXXXII) in the usual way using ethyl vinyl ether with subsequent hydrolysis of the ether-acetal (LXXXIII) and the simultaneous removal of the methoxy-group led, however, to 7-cyanohepta-2,4,6-trien-1-al (LXXXIV, n = 3), which was fully in the *trans*-configuration as a result of isomerisation during the chain growth process and hydrolysis. It is noteworthy that the hydrolysis of the mixture of the *cis-trans*-isomers of compound (LXXXII) also gave a product which was fully in the *trans*-configuration:

$$(CH_3O)_2CHCH{=}CHCHO \rightarrow \underset{(LXXXII)}{NC(CH{=}CH)_2CH(OCH_3)_2} \rightarrow$$
$$\rightarrow \underset{(LXXXIII)}{NC(CH{=}CH)_2CH(OCH_3)CH_2CH(OCH_3)(OC_2H_5)} \rightarrow \underset{(LXXXIV,\ n=3)}{NC(CH{=}CH)_nCHO}.$$

Compound (LXXXIV, n = 4) was obtained by the reaction of the octatrienedial (XLIII, n = 3) with an equimolar amount of cyanomethylenetriphenylphosphorane[72]. A general method was thus developed and aldo-nitriles and their acetals have become readily accessible.

Aldo-Ketones and Their Acetals

The method of synthesis of the acetals of aldo-ketones was outlined using as an example the reaction of the monoacetal of fumaric dialdehyde with acetylmethylenetriphenylphosphorane, where the dimethyl acetal of 6-formylhexa-3,5-dien-2-one (LXXXV) was obtained in high yield[25]:

$$(CH_3O)_2CHCH{=}CHCHO + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOCH_3 \rightarrow \underset{(LXXXV)}{(CH_3O)_2CH(CH{=}CH)_2COCH_3}.$$

The reaction of equimolar amounts of the octatrienedial (XLIII, n = 3) with acetylmethylenetriphenylphosphorane was used for the preparation of 10-formyldeca-3,5,7,9-tetraen-2-one[72]:

$$(XLIII,\ n=3) + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOCH_3 \rightarrow OHC(CH{=}CH)_4COCH_3.$$

Esters of Keto-Acids

The hydration of hepta-2,4-dien-6-ynoic acid by heating with dilute sulphuric acid in the presence of mercury sulphate[52] leads to 6-oxohepta-2,4-dienoic acid:

$$HC{\equiv}CCH{=}CHCH{=}CHCOOH \rightarrow CH_3CO(CH{=}CH)_2COOH.$$

When the starting compounds are available, this method can be used in principle for the synthesis of keto-acids. When aldo-esters are available, the synthesis of esters of polyene keto-acids by the reaction between acetylmethylenetriphenylphosphorane and aldo-esters becomes of general importance. The ethyl esters of the keto-acids (LXXXVI) were obtained in this way[25,72]:

$$C_2H_5OOC(CH{=}CH)_nCHO + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOCH_3 \rightarrow \underset{(LXXXVI)}{C_2H_5OOC(CH{=}CH)_3COCH_3}.$$

Esters of Cyano-Acids

The general method for the synthesis of esters of cyano-acids (LXXXVII) is based on the reaction of cyanomethylenetriphenylphosphorane or diethyl cyanomethylphosphonate with esters of aldo-acids (LXXXI)[25,72,73]:

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCN + (LXXXI) \rightarrow \underset{(LXXXVII)}{NC(CH{=}CH)_nCOOC_2H_5}.$$

In addition, esters of cyano-acids have been obtained in high yields by the reaction of aldo-nitriles (LXXXIV) with diethyl esters of ethoxycarbonylmethylphosphonic acid (or the corresponding phosphorane)[72,73]:

$$(\text{LXXXIV}) + (C_2H_5O)_2P(O)CH_2COOC_2H_5 \rightarrow (\text{LXXXVII}).$$

The compounds formed are fully in the *trans*-configuration.

Esters of Nitro-Acids

The general method for the synthesis of these esters[74] is based on the condensation of aldo-acid esters with nitromethane followed by the dehydration of the hydroxynitro-compounds (LXXXVIII) formed:

$$\underset{(n=0-3)}{C_2H_5OOC(CH{=}CH)_nCHO} + CH_3NO_2 \rightarrow \underset{(\text{LXXXVIII})}{C_2H_5OOC(CH{=}CH)_nCH(OH)CH_2NO_2} \rightarrow \underset{(\text{LXXXIX})}{\rightarrow C_2H_5OOC(CH{=}CH)_{n+1}NO_2}.$$

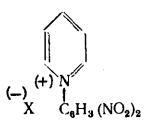
To achieve the dehydration, the hydroxynitro-compounds (LXXXVIII, n = 0–2) are converted into halogenonitro-derivatives, which can be dehydrohalogenated by treatment with sodium acetate, without isolation. In the synthesis of the ethyl ester of ω-nitronona-2,4,6,8-tetraenoic acid (LXXXIX, n = 3) it is best to carry out the dehydration directly by passing the compound down an alumina column. The yields of the nitro-acid esters are satisfactory. The nitro-esters (LXXXIX, n = 1–3) of the *trans*-series, which were formerly unknown, were obtained in this way.

Amino-Aldehydes

A general method for the synthesis of ω-dimethylamino-polyenals (XC) and ω-*N*-methyl-*N*-phenylpolyenals (XCI) with fairly high yields (50–70%) has been described[75-77]:

$$\underset{(\text{XCII})}{[RR'N(CH{=}CH)_nCH{=}NRR']X} \xrightarrow{OH^-} \underset{\substack{(\text{XC},R=R'=CH_3)\\(\text{XCI},R=CH_3;\ R'=C_6H_5)}}{RR'N(CH{=}CH)_nCHO}.$$

However, a general procedure for the synthesis of compounds (XCII) has not been developed. Thus compound (XCII, n = 2) is most conveniently obtained by the reaction of secondary amines with an alcoholic solution of 1-(2′,4′-dinitrophenyl)pyridinium halide at 60–70°:[76,77]



$$\xrightarrow{RR'NH} (\text{XCII}, n = 2).$$

Compound (XCII, n = 3) can be obtained by the reaction[75]:

$$\underset{(n=2)}{(\text{XC}) \text{ or } (\text{XCI})} \xrightarrow[H^+]{HC{\equiv}CMgBr} HC{\equiv}C(CH{=}CH)_2CHO \xrightarrow[RR'NH\cdot HClO_4]{RR'NH} (\text{XCII}, n = 3, X = HClO_4).$$

For this purpose, the amino-aldehyde (XC, n = 2) or (XCI, n = 2) is allowed to react with ethynylmagnesium bromide, after which the product is hydrolysed with sulphuric acid. The resulting hepta-2,4-dien-6-ynal is treated with a mixture of dimethylamine and dimethylammonium perchlorate or of *N*-methylaniline and *N*-methylanilinium perchlorate, compounds (XCII, R = R′ = CH, n = 3) (yield 38%) or (XCII, R = CH_3, R′ = C_6H_5, n = 3) (yield 93%) being obtained.

Finally the following synthetic procedure has been developed for compounds of the series (XCII, n = 4–6, X = $HClO_4$)[75]:

$$\underset{(n=2-4)}{(\text{XCI})} \xrightarrow[2.\ H^+]{1.\ CH_3OCH{=}CHC{\equiv}CMgBr} \underset{(\text{XCIII})}{CH_3OCH{=}CHC{\equiv}C(CH{=}CH)_nCHO} \xrightarrow{H_2} \underset{(\text{XCIV})}{CH_3O(CH{=}CH)_{n+2}CHO} \xrightarrow[RR'NH\cdot HClO_4]{RR'NH} (\text{XCII}, n = 4-6, X = HClO_4).$$

The amino-aldehydes (XCI, n = 2–4) are condensed with 1-methoxybut-2-en-4-ynylmagnesium bromide, the product is hydrolysed with a solution of tartaric acid, and the resulting enyne methoxy-aldehydes (XCIII) are hydrogenated in the presence of Lindlar's catalyst. Treatment of the unstable polyene methoxy-aldehydes (XCIV) with secondary amines and the corresponding perchlorates yields the required compound (XCII). The above reaction constitutes at the present time the only way of synthesising compounds of this type. Despite the satisfactory yields at all stages, this procedure is inconvenient because of the large number of stages involved.

Amino-Acid Esters

The Wittig reaction between amino-aldehydes and diethyl ethoxycarbonylmethylphosphonates has been proposed for the synthesis of amino-acid esters[73]. For example:

$$(\text{XCI}, n = 2) + (C_2H_5O)_2P(O)CH_2COOC_2H_5 \rightarrow RR'N(CH{=}CH)_3COOC_2H_5,$$

where the yield is 40% for R = R′ = CH_3 and 70% for R = CH_3 and R′ = C_6H_5. Isomers which are fully in the *trans*-configuration are formed.

Hydroxy-Aldehydes

The hydroxy-aldehydes of the polyene series are the enol forms of dialdehydes of the type of glutaconic aldehyde and are known in the form of salts and benzoates (XCV). The sodium salts of hydroxy-aldehydes (XCVI, n = 1–3) are formed on heating dimethylaminopolyenals (XC) with aqueous methanolic sodium hydroxide solution[75]:

$$(\text{XC}) \rightarrow \underset{(\text{XCVI})}{NaO(CH{=}CH)_nCHO}.$$

The salts (XCVI, n = 1, 2) are formed in 90–95% yields, while the yield of the salt (XCVI, n = 3) is low. The dimethylaminopolyenal (XC, n = 4) does not hydrolyse under these conditions at all. Although the compounds (XC, n = 3, 4) are capable of undergoing hydrolysis on heating with a solution of potassium hydroxide in a mixture of water and 1-methylpyrrolidone, the compounds (XC, n = 5, 6) are no longer hydrolysed under these conditions. The change in the reactivity of dimethylaminopolyenals (XC) with increase in the number of double bonds can be explained by the weakening of the electronic effect (+M-effect) of the dimethylamino-group of the aldehyde group with increasing chain length:

$$\underset{(\text{XC})}{(CH_3)_2\ddot{N}{-}(CH{=}CH)_n{-}CH{=}O}.$$

The benzoates (XCV) are formed when benzoyl chloride is allowed to react with pyridine solutions of potassium salts of hydroxy-aldehydes[75]:

$$\underset{(n=2,3,4)}{KO(CH{=}CH)_nCHO} + C_6H_5COCl \rightarrow \underset{(\text{XCV})}{C_6H_5COO(CH{=}CH)_nCHO}.$$

ωω-Dichloro-Aldehydes

A number of unbranched ωω-dichloropolyenals (XCVII) have been described[78,79]. In their synthesis the readily available ωω-dichloroacrolein is converted into an acetal which is then allowed to react with ethyl vinyl ether, according to the general procedure for the synthesis of polyenals:

$$Cl_2C{=}CHCH(OC_2H_5)_2 \xrightarrow{CH_2{=}CHOC_2H_5} Cl_2C{=}CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2 \xrightarrow{H^+} \rightarrow Cl_2C{=}CHCH{=}CHCHO \xrightarrow{HC(OC_2H_5)_3} Cl_2C{=}CHCH{=}CHCH(OC_2H_5)_2 \rightarrow \rightarrow Cl_2C{=}CH(CH{=}CH)_nCHO.$$

(XCVII)

The chain growth reaction is performed in the presence of zinc chloride and boron trifluoride-ether and the hydrolysis is carried out by heating with a 15% solution of sodium acetate in 85% acetic acid: ωω-dichloropolyenals (XCVII, n = 1–4) are obtained in a yield of 70–90%.

ωω-Dichloro-Alcohols

A series of ωω-dichloropolyene alcohols (XCVIII) have been obtained[79] by the reduction of ωω-dichloropolyenals (XCVII) with lithium aluminium hydride (yield 40–50%):

$$(XCVII) \rightarrow Cl_2C{=}CH(CH{=}CH)_nCH_2OH.$$
$$(XCVII),\ n = 1{-}4)$$

ωω-Dichloro-Acids

ωω-Dichloropolyene acids (XCIX) have been obtained by the oxidation of ωω-dichloropolyenals (XCVII) with silver oxide[78], the yield being 30–37%:

$$(XCVII) \rightarrow Cl_2C{=}CH(CH{=}CH)_nCOOH.$$
$$(XCIX)$$

In addition, another method has been proposed for the synthesis of these acids[73]. In this procedure ωω-dichloropolyenals (XCVII) are converted into esters of ωω-dichloro--acids (C) by reaction with the diethyl ester of ethoxycarbonylmethylphosphonic acid and then compound (C) is subjected to alkaline hydrolysis, which results in a high yield of ωω-dichloro-acids (XCIX) containing one double bond more than the initial ωω-dichloropolyenals (XCVII):

$$(XCVII) + (C_2H_5O)_2P(O)CH_2COOC_2H_5 \rightarrow \underset{(C)}{Cl_2C{=}CH(CH{=}CH)_{n+1}COOC_2H_5} \rightarrow (XCIX).$$

It is quite evident from the data presented above that a wide variety of polyenes with different substituents at the ends of the chain have now become accessible.

IV. SOME PROPERTIES OF POLYENES

Those properties of substituted polyenes with different functional groups which have been investigated to elucidate the effect on them of the length of the polyene chain or the effect on the properties of the functional group due to the substituents in the ω-position will be considered in this section. It is noteworthy that in the literature there still persists a quite definite view on this subject, which arose as a result of a comparison of the reactivities of saturated compounds, on the one hand, and of mono-olefins and dienes, on the other. In the first place this view is in conflict with the well known and long established analogy between the behaviour of certain saturated and unsaturated compounds in reactions, which gave rise to the concept of vinylogy — the transfer of the mutual influence of atoms along a system of conjugated double bonds, the concept having now become firmly established in organic chemistry. The principle of vinylogy proved very fruitful and made it possible to explain many facts. However, within the framework of synthetic chemistry the limits of the application of this principle to the series of aliphatic conjugated polyenes have not been investigated and it has been assumed *a priori* that the principle of vinylogy is applicable to all $X(CH{=}CH)_nY$ systems, regardless of the chain length and the structure of the end groups. This hypothesis is still to be found in monographs and text books on theoretical organic chemistry.

Wide acceptance of this view has been favoured both by studies of the properties of $X(CH{=}CH)_nY$ systems, where n = 1 or 2 or X and Y are the conjugated groups (as in cyanine and polymethine dyes), and the results of the first quantum-mechanical calculations, which showed that, when the length of the polyene chain increases, an equalisation of bond orders and hence of the lengths of double and single bonds apparently takes place. However, the use of various methods (the molecular orbital–linear combination of atomic orbitals method, the valence bond method, and the free electron method) in subsequent quantum-mechanical calculations demonstrated unambiguously that in the ground electronic state polyenes are systems with an alternating charge density, the density maxima corresponding to the double bonds in the classical formula.

We shall examine further the results of studies on the transfer of the mutual influence of atoms along the chain.

Polarographic Reduction of Polyenes

The polarographic reduction of the polyenals $CH_3(CH{=}CH)_nCHO$ (n = 1–5)[80–82] in aqueous dioxan buffer solutions has been investigated in the pH range 1–11. The dependence of the half-wave potential and the ratio $id/Cm^{2/3}t^{1/6}$ on the pH of the medium and the number of double bonds has also been studied. The investigators adopted the following mechanism for the reduction at a dropping mercury electrode:

$$CH_3(CH{=}CH)_nCHO + H^+ + e \rightleftarrows CH_3(CH{=}CH)_n\dot{C}HOH \rightarrow \rightarrow CH_3(CH{=}CH)_nCH(OH)-CH(OH)(CH{=}CH)_nCH_3.$$

In the range pH 1–11 one distinct polarographic wave was observed and, over a narrower pH range, a second wave of the same height as the first occurred at pH values which were lower the greater was the number of double bonds. The ratio $id/Cm^{2/3}t^{1/6}$ for the first and second waves is approximately the same and independent of the pH and the number of double bonds. The half-wave potentials of both waves are displaced towards less negative potentials with increase in the number of double bonds, the increment per double bond becoming smaller as the chain length increases. Thus the difference between the half--wave potentials of crotonic and sorbic aldehydes is 0.23 V, while that between the values for deca-2,4,6,8-tetraenal and dodeca-2,4,6,8,10-pentaenal is only 0.07 eV. The same has also been found for the half-wave potential of the second wave.

Thus accumulation of double bonds facilitates the polarographic reduction of polyenals, but the introduction of each new double bond makes an increasingly smaller contribution to the polarographic behaviour of the molecule. The diffusion coefficient D of polyenals, calculated from the Ilkovič equation, also tends to decrease to a definite limit:

n	1	2	3	4	5
D, 10^6 cm^2 s^{-1}	6.1	5.3	5.1	4.3	4.2.

Dipole Moments of Polyenes

The dipole moments of the dimethylaminopolyenals $(CH_3)_2N(CH{=}CH)_nCHO$ (n = 0–4) in benzene solution have been determined at 25° [83] and the following values (dipole moments μ in Debye units) have been found:

n	0	1	2	3	4
μ	3.86	6.24	7.62	8.24	8.50.

It is evident that the dipole moments increase with chain length, but the difference between the values of μ for adjacent members decreases, i.e. the dipole moment tends to a limit.

On the basis of the data obtained and the calculation of the charge transfer from end to end along the system of conjugated double bonds using various stereochemical models, it was concluded [83] that each end-group has a restricted sphere of action, extending approximately over three double bonds.

Infrared Spectra

Infrared spectroscopy is widely used to characterise substituted polyenes with different functional groups (see, for example, Lapitskii et al. [56]), but few papers dealing with the effect of the number of double bonds or the relative positions of the functional groups on the infrared spectra of polyenes have been published. In 1948 the infrared spectra of the dimethylpolyenes $CH_3(CH{=}CH)_nCH_3$ (n = 2–6), the polyenals $R(CH{=}CH)_nCHO$ (R = CH_3, α-furyl, n = 1–4), and the corresponding azines were investigated in the range 1440–1900 cm^{-1} to elucidate the effect of the accumulation of conjugated double bonds on absorption in the region corresponding to double bond vibrations. On the basis of their data, the investigators concluded that the vibration bands associated with the double bonds are displaced towards lower frequencies with increase in the number of double bonds, the charge per double bond decreasing with the number of such bonds [84].

The infrared spectra of compounds of the type $X(CH{=}CH)_nCOOC_2H_5$ with all the double bonds in the *trans*-configuration, where X = CH_3 (n = 1–4), $COOC_2H_5$ (n = 1–7), CHO (n = 1–4), NO_2 (n = 1–4), and OC_2H_5 (n = 1, 2), were investigated recently [85], special attention being devoted to the problem of the mutual influence of the end-groups via the system of conjugated double bonds. The CO stretching frequencies in the spectra of these compounds are presented in Table 1 as a function of the number of double bonds. Table 1 shows that in the spectra of the compounds investigated the CO stretching frequencies due to the ethoxycarbonyl group approach one another as the length of the polyene chain increases: the maximum differences between the frequencies amount to 24 cm^{-1} for n = 1, 16 cm^{-1} for n = 2, 7 cm^{-1} for n = 3, and only 3 cm^{-1} for n = 4. Hence the authors concluded that the mutual influence of atomic groups in the ground electronic state of the molecule decays rapidly with increase in the length of the intervening chain of conjugated bonds.

TABLE 1. CO vibration frequencies in the compounds $X(CH{=}CH)_nCOOC_2H_5$ (in carbon tetrachloride, values of ν in cm^{-1}).

n	R					
	CH_3	NO_2	CHO		$COOC_2H_5$	OC_2H_5
1	1724	1735	1733	1704	1730	1711
2	1718	1727	1725	1695	1721	1711
3	1714	1721	1718	1688	1715	
4	1715	1717	1716	1688	1714	
5					1713	
6					1713	
7					1714	

It has also been established that the intensity of the infrared absorption bands in the region of 1600 cm^{-1} (vibrations of the polyene chain) is determined mainly by the number of double bonds (increasing with the latter) involved in the vibrations, the relation between the absolute integral intensity of the absorption bands in the region of 1600 cm^{-1} and the number of double bonds being linear. On the basis of the experimental data and a comparison of the experimental and calculated relative intensities of the absorption bands in the region of 1600 cm^{-1}, it was concluded [85] that there is an alternation of charges at carbon atoms along the polyene chain.

Yukhnovski [86], who compared the frequencies and the integral intensities associated with the nitrile group in β-phenyl-substituted trans-α-cyanostilbenes and the corresponding benzonitriles, also concluded that the effect of substituents on the frequency and integral intensity of the band due to the nitrile group in compounds of the type *trans*-$RC_6H_4CH{=}CH(C_6H_5)CN$ weakens with increase in the length of the conjugation chain.

Raman Spectra

The Raman spectra of the diethyl esters of the polyene-$\alpha\omega$-dicarboxylic acids $C_2H_5OOC(CH{=}CH)_nCOOC_2H_5$ (n = = 1–8) have been analysed [87]. The frequencies ω of the most intense lines of the Raman spectra of acetone solutions of these compounds are presented in Table 2 (exciting light–the Hg*e* mercury blue line, frequency μ = 22 938 cm^{-1}). The lines with the frequencies ω_1 and ω_2 characterise the vibrations of the polyene chain and the line with the frequency ω_3 characterises the behaviour of the carbonyl group. The spectra of the diesters with n = 6–8 contain overtones, because these absorption bands and the exciting lines occur in the resonance region.

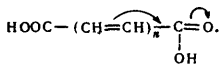
TABLE 2. Principal frequencies (in cm^{-1}) of the Raman spectra of $C_2H_5OOC(CH{=}CH)_nCOOC_2H_5$.

n	ω_1	ω_2	ω_3	n	ω_1	ω_2
1	1210	1664	1733	5	—	1570
2	1135	1644	1726	6	1142	1562
3	1139	1621	1721	7	1140	1550
4	1139	1596	1717	8	1137	1540

Analysis of the vibration frequencies of the polyene diesters led to the conclusion[87] that, in the first place, there is a comparatively small change in the vibration frequencies of the polyene chain as its length increases and examination of compounds in the range from $n = 3$ to $n = 8$ shows that in long chains of conjugated double bonds there is no appreciable "equalisation" of the multiple bonds. In the second place, since with increase in chain length the addition of each new unit has a smaller effect on the frequencies, the mutual influence of the atomic groups becomes weaker as the length of the intervening chain of conjugated double bonds becomes greater.

pK_a Values of Polyenoic Acids

To elucidate the effect of electron-acceptor substituents on the pK_a values of polyenoic acids, the latter were determined for $CH_3(CH=CH)_nCOOH$ and $HOOC(CH=CH)_nCOOH$ ($n = 1-4$).[88] The data obtained are presented in Table 3. The lower pK_a values of dicarboxylic acids compared with the monocarboxylic acids when $n = 1$ and 2 can be explained by the enhanced acidity of the dicarboxylic acid due to the $-M$-effect of the second carbonyl group:



The appreciable increase of the pK_a on going from muconic acid to octa-2,4,6-triene-1,8-dioic acid indicates a weakening of the $-M$-effect, i.e. a rapid decay of the effect of the electron-acceptor carboxy-group on the pK_a.

Ultraviolet Spectra

The relation between the length of the polyene chain and the positions and intensities of the bands in the electronic absorption spectra has attracted the attention of investigators for a long time. The studies in this field were made in 1935 by Hausser and Kuhn[89-92], who investigated the ultraviolet spectra of the polyenals $CH_3(CH=CH)_nCHO$ ($n = 1-3$), the polyenemonocarboxylic acids $CH_3(CH=CH)_nCOOH$ ($n = 1-4$), α-furylpolyenals and α-furylpolyenoic acids ($n = 1-3$), and also the diphenylpolyenes $C_6H_5(CH=CH)_nC_6H_5$ ($n = 1-7$). It was established that (1) the introduction of each new double bond causes a shift of the band towards the visible part of the spectrum and (2) the magnitude of the shift decreases with the number of double bonds.

Subsequently the ultraviolet spectra of polyenes were investigated by a number of workers. Thus one may refer to the work of Blout and Fields[93], who investigated the polyenals $CH_3(CH=CH)_nCHO$ ($n = 1-7$), the dimethylpolyenes $CH(CH=CH)_nCH_3$ ($n = 1-7$), the ω-furylpolyenals ($n = 0-6$), and certain azines. In other investigations dimethylpolyenes[94-96], *NN*-dimethylaminopolyenals[75], ferrocenylpolyenes[97], etc. were studied. All these investigations confirmed the principal conclusions of Hausser and Kuhn. Furthermore, a comparative study of the spectra of ω-dimethylaminopolyenals, the sodium salts of ω-hydroxypolyenals, and $[(CH_3)_2N(CH=CH)_nCH=N(CH_3)_2]HClO_4$ led to the conclusion[75] that the spectra of the linear polyenes $X(CH=CH)_nY$ differ in principle from the spectra of polyene cyanine dyes and from the spectra of polyene molecules with charges at the end of the chain, of the type $\bar{O}(CH=CH)_nCHO$.

TABLE 3. pK_a values for certain polyenoic acids (in 50% aqueous alcohol).

n	$CH_3(CH=CH)_nCOOH$ pK_a	$HOOC(CH=CH)_nCOOH$ pK_{a_1}
1	4.66	2.98
2	4.62	2.70
3	5.37	5.01
4	5.42	5.11

There exist very numerous data on the ultraviolet spectra of isoprenoids with different functional groups, such as vitamin A and carotenoids, because the spectra are widely used to characterise compounds of this kind. However, the presence of methyl side-groups and in many cases the complexity of the end-groups make the interpretation of the optical properties difficult, but several empirical equations relating the position of the absorption bands to the structure of polyenes of this kind have been postulated[98-100]. In this connection we shall examine the studies dealing with unbranched polyenes with different functional groups. Table 4 lists the principal absorption maxima of the unbranched polyenes.

Analysis of the ultraviolet spectra of linear polyenes led to the following conclusions[101].

1. The replacement of the methyl group in a dimethylpolyene by an electron-donor or an electron-acceptor substituent causes a bathochromic shift, which increases in the following sequence of substituents:

$$OC_2H_5 < COOC_2H_5 < CHO \leqslant COCH_3 < NO_2.$$

TABLE 4. Principal absorption maxima of polyenes (solvent – alcohol, other solvents indicated in brackets, literature references indicated in footnotes).

X	Y	n = 1	2	3	4	5	6
		$X(CH=CH)_nX$					
CH_3		—	227[a]	263[b]	307[a]	343[c]	374[a]
CN[a]		—	259[d]	297	330	379	—
$COOC_2H_5$[a]		210	264	303	335	365	391
CHO[a]		225[e] (iso-octane)	269[c]	317	352	388	—
$COOH_3$[a]		226[g]	276[g]	—	351	380.5	406
COC_6H_5[a]		—	—	—	385	415	
X	Y	n = 1	2	3	4	5	
		$X(CH=CH)_nY$					
CH_3	$CCOC_2H_5$[a]	206	258	301	334	365	
CH_3	CHO[a]	218	272	315	351	380	
CH_3	$COCH_3$	220[h]	273.5[a]	316[i]	351[i]	—	
CH_3	NO_2[j]	229	309				
CHO	$COOC_2H_5$[a]	208	268	309	341	—	
CHO	CN[a]	—	263	305	—	—	
CHO	$N(CH_3)_2$[k]	287[a]	361.5	421.5	462.5	491.5	
			(methylene chloride)				
$COOC_2H_5$	CN[a]	—	—	299	332	—	
$COOC_2H_5$	$COCH_3$[a]	—	—	310	—	—	
$COOC_2H_5$	NO_2[a]	222	281	327	363	—	
$COOC_2H_5$	OC_2H_5[a]	231	289	—	—	—	
$COOC_2H_5$	$N(CH_3)_2$[l]	—	—	394	—	—	
$COOC_2H_5$	$Cl_2C=CH$[l]	270	302	332	—	—	

[a]Ref. 101; [b]Ref. 93; [c]Ref. 102; [d]Ref. 103; [e]Refs. 104 and 105; [f]Ref. 106; [g]Ref. 107; [h]Ref. 108; [i]Ref. 109; [j]Ref. 110; [k]Ref. 74; [l]Ref. 73.

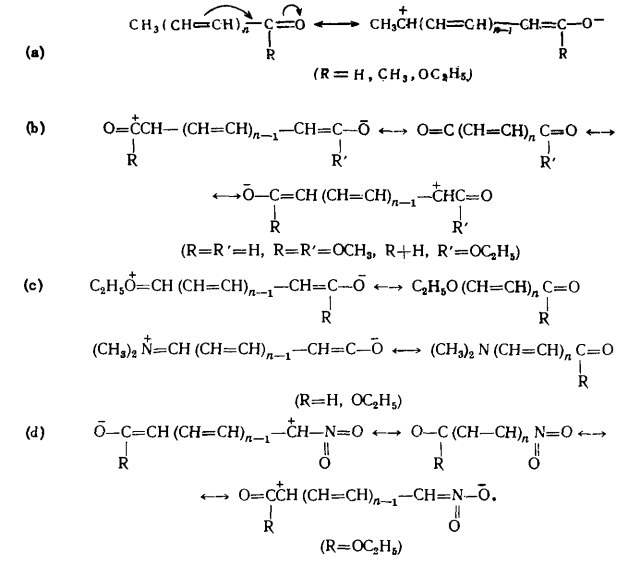
2. The replacement of the methyl group in the series $CH_3(CH=CH)_nR$, where R = CHO or $COOC_2H_5$, by electron-acceptor groups in which one carbon atom is linked by a multiple bond to the atom of another element (CHO, $OCCH_3$, $COOC_2H_5$, CN) gives rise to very slight hypsochromic or bathochromic shifts, whose absolute magnitude does not exceed 10 nm (see also Refs. 111 and 112).

3. The replacement of the methyl group in CH_3. $.(CH=CH)_nCOOC_2H_5$ by the nitro-group results in an appreciable bathochromic shift (30–59 nm).

4. The replacement of the methyl group in the series $CH_3(CH=CH)_nR$, where R = CHO or $COOC_2H_5$, by an electron donor group causes an appreciable bathochromic shift (29–75 nm).

In the last two cases the bathochromic shift increases as the double bonds accumulate.

The observed features were explained by the nature of the polarisation of the molecules in the excited state[101]:



In case (a) the electrons in the molecule in the excited state are displaced in the direction indicated by the arrow and therefore the introduction of the CO group is equivalent to the introduction of yet another double bond. When a second chromophore of the type of CO is introduced into the ω-position in the molecule, simultaneous polarisation of both CO groups is unlikely and therefore the observed displacement of the band is similar to that which occurs on introduction of a single substituent [case (b)]. In case (c) the free electron pair of nitrogen or oxygen participates in conjugation, which makes a considerable contribution to the excited state of the molecule, the mobility of the electrons of the auxochromes and the decrease of the polarisation energy becoming more pronounced as the chain length increases. Finally, as a result of the considerable difference in the polarisation energies of the ethoxycarbonyl and nitro-groups, in case (d) polarisation probably occurs preferentially at the group for which the polarisation energy is smaller, which can alter the principal absorption maximum, compared with the corresponding monosubstituted polyenes.

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UBIQUINONES (COENZYME Q)

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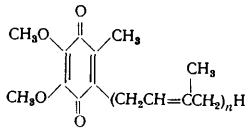
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The studies carried out in recent years demonstrate the outstanding role of substituted quinones, ubiquinones (coenzyme Q) (I), in intracellular electron transport coupled with oxidative phosphorylation [1-8]:



(I)

The data on this new group of coenzymes are collected in the present review and certain hypotheses concerning the participation of quinones in intermediate reactions in oxidative phosphorylation are considered.

I. DISCOVERY AND NATURAL SOURCES OF UBIQUINONES

At the end of 1955 a group of investigators at the University of Liverpool carried out experiments designed to elucidate the mechanism of the effect of vitamin A in growth processes and in cases of xerophthalmia [9]. They isolated from the mucus membrane of the horse intestine a substance, the spectrum of which had characteristic absorption maxima at 272 and 400 nm. [10,11] Somewhat later the same investigators isolated chromatographically from the non-hydrolysable fraction of liver lipids and other mammalian tissues (under normal conditions and under conditions of vitamin A deficiency) other analogous fractions which were denoted by the letters SA, SB, and SC. [12-16] It was further elucidated that the substance in fraction SA is identical with that isolated from the intestine and that it is indeed present in human and animal liver, kidneys, spleen, blood, and pancreas and is localised within the cell [17-22]. It was established that the substance of the fraction SA contains a cyclic group of the quinone type and a side-chain with a definite number of double bonds. The compound was given the name "ubiquinone", which indicates its chemical type and wide distribution in nature [17,18,20].

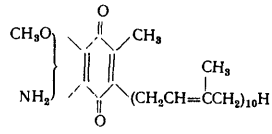
Simultaneously with the investigations in Liverpool, Swiss chemists of the Hofmann-La Roche Company [23,24] isolated two ubiquinones from pig heart and from yeast after processing a large amount of natural material. The first ubiquinone had a side-chain of ten isoprenoid units in position 6 — ubiquinone(50) or UQ_{10} — and the second a side-chain of six isoprenoid units — ubiquinone(30) or UQ_6. Soon the same investigators achieved the synthesis of UQ_6 and UQ_{10} and also of their homologue UQ_9 and showed that these quinones are identical with the natural compounds [24,25].

In 1957 yet another group of investigators, from Wisconsin University, published their work on the isolation from beef heart mitochondria of a substance with properties characteristic of quinones and called coenzyme Q_{275} (quinone with an ultraviolet absorption maximum at 275 nm) [26,27]. Soon, in collaboration with the American chemists of the Merck Company (New Jersey), the investigators from Wisconsin demonstrated the identity of coenzyme Q_{275} with the ubiquinones discovered by the workers of the Liverpool school and in Switzerland [28-30].

At the Fourth International Biochemical Congress in Vienna in 1958 the reports of all the groups of investigators were presented and the identity of the compounds confirmed. In 1961 the Committee on Enzymes of the International Biochemical Union [31] recommended the name "ubiquinone" to unify the terminology for this class of substances, in view of the fact that the nature of this cofactor had already been established.

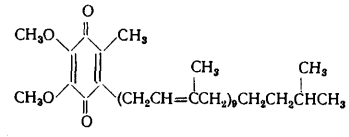
Natural ubiquinones (UQ_6, UQ_7, UQ_8, UQ_9, and UQ_{10}) have been found in various tissues of animals [10-13,15,16,19,24-26,32-38] and plants [39,40] and in micro-organisms [23,28,41-46]. UQ_6, [23,28,45,46] UQ_7, [28,45,47] and UQ_8 [28,45,47] are encountered almost exclusively in micro-organisms, only traces being found in animals [47]. UQ_9 [25,28,37,38,40,45,47] and particularly UQ_{10} [11,14,21,24-26,34-41,44,45,47] are distributed mainly in animals and in higher plants [48], and UQ_9 is found in vegetable oil [30] and in aloe [37]. The heart tissue of rhesus monkeys contains UQ_{10}. These animals are suitable objects for UQ_{10} tests in various diseases. UQ_{10} has been found in the nerve tissue of the frog. This fact can be used in the investigation of the role of UQ_{10} in neurology. UQ_{10} has also been found in tumour tissues in man and in rodents [49]. In man UQ_{10} has been isolated from heart tissue and other organs [38,50]. A comparative estimate of the content of ubiquinone(50) in various organs showed that the organism of the adult man contains 0.5–1 g of UQ_{10}.

Micro-organisms are capable of synthesising all the natural homologues of ubiquinones (UQ_6–UQ_{10}). [24,28,38,45] The cells of *Ochromonas mathamensis* produce UQ_{10} and those of *Polyporous schweinitzii* both UQ_9 and UQ_{10}. [49] An analogue of UQ_{10}, rhodoquinone with one free amino-group (II), [51] has been isolated from a culture of *Rhodospirillum rubrum*:



(II)

Another representative of the group of ubiquinones has been isolated from the cells of *Gibberella fujckuroi* and *Penicillum stipitatum* [52,53]. Identification of this compound, obtained from two types of culture, showed that the tenth isoprenoid residue of the side-chain is saturated. This new compound, called UQ_{10}(H-10), has the structure (III): [53-55]

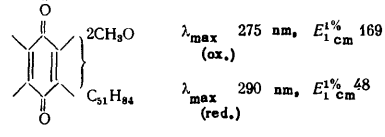


(III)

II. DETERMINATION OF THE STRUCTURE OF UBIQUINONES

1. Ubiquinone(50) (UQ_{10})

The general formula found [29] for UQ_{10} is $C_{59}H_{90}O_4$; the following partial formula (IV) has been put forward on the basis of the displacement of the ultraviolet maximum from 275 to 290 nm after reduction under mild conditions:



(IV)

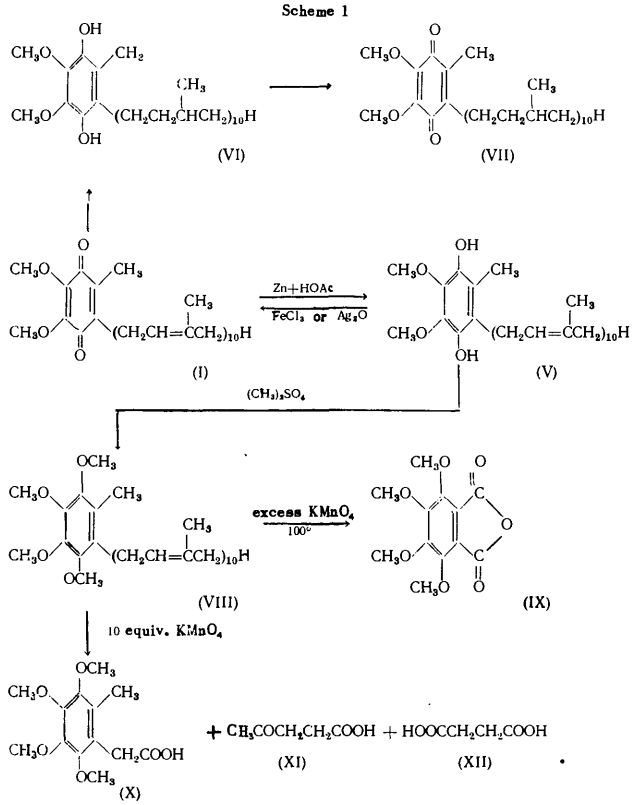
Determination of the O–Alk residues showed the presence of two methoxy-groups. Since it was suggested that the UQ_{10} molecule contains the benzoquinone ring, the two CH_3O groups could occupy three different positions. Comparison of the ultraviolet spectra of UQ_{10} in the quinone and

hydroquinone forms with those of aurantiogliocladin[56] (2,3-dimethoxy-5,6-dimethyl-1,4-benzoquinone) revealed their close similarity. However, on the basis of these data, one cannot finally conclude that UQ_{10} is a derivative of 2,3-dimethoxy-5-methylbenzoquinone, because the ultraviolet spectra of 2,6-dimethoxy-3,5-dimethyl- and 2,5-dimethoxy-3,6-dimethyl-1,4-benzoquinones[57,58] differ only slightly from the ultraviolet spectra of the isomeric aurantiogliocladin.

Chemical conversions (Scheme 1) suggested that one of the substituents in the *p*-quinone ring of UQ_{10} is a polyisoprenoid chain[28,29]: on catalytic reduction of UQ_{10}, 11 moles of hydrogen are absorbed; eicosahydroquinone (VI) is formed and after oxidation is converted into eicosahydro-UO_{10} (VII). Oxidation of UQ_{10} with alkali and potassium permanganate leads to the formation of levulinic, acetic, and succinic acids. The isoprenoid nature of the side-chain of UQ_{10} has been confirmed by nuclear magnetic resonance[59] and a difference between the protons of the methyl groups of the ring and the isoprenoid chain has been demonstrated. Together with other evidence, the NMR data confirm to a large extent (but do not provide the final proof) the positions of the two CH_3O groups, one CH_3 group, and of the isoprenoid chain of ten units.

The positions of all the substituents in the quinone ring of UQ_{10} were finally demonstrated by oxidative degradation. Dimethylhydro-UQ_{10} (VIII) was obtained in a crystalline form by the reduction of UQ_{10} (I) to the hydroquinone (V) and exhaustive methylation. Oxidation of compound (VIII) with potassium permanganate in aqueous alkaline solution at 100° gave, after sublimation, tetramethoxyphthalic anhydride (IX). Oxidation of compound (VIII) with potassium permanganate in acetone gave 2-methyl-3,4,5,6-tetramethoxyphenylacetic (X), levulinic (XI), and succinic (XII) acids.

Scheme 1



Another group of investigators, who studied independently the structure of UQ_{10},[9,24] subjected ubiquinone(50) to reductive acetylation followed by oxidative degradation of diacetylhydro-UQ_{10} and isolated acetone and levulinic aldehyde in the form of 2,4-dinitrophenylhydrazones and also 3,6-diacetoxy-4,5-dimethoxy-2-methylphenylacetic acid, which was characterised via its *p*-toluidide derivative.

Thus chemical conversions and spectroscopic data carried out by different investigators showed that UQ_{10} is 2,3-dimethoxy-5-methyl-6-[3-methyl-2-butenylenakis--(3-methyl-2-butenylene)]-1,4-benzoquinone.

2. Ubiquinones(30), (35), (40), and (45) (UQ_6–UQ_9)

The ultraviolet spectra of various natural ubiquinones[60] are the same, but the extinction coefficient is inversely proportional to the length of the carbon chain (decrease of the mole fraction of the chromophore). Qualitatively the infrared spectra of ubiquinones are also the same[24]. Each of the natural ubiquinones is characterised by a different value of R_f in paper and thin-layer chromatography[61,62] and also by a different redox potential[63,64]. The molecular weight of ubiquinone homologues has been determined by the esterification of the OH group of the corresponding [^{14}C]-ubiquinols with acetic anhydride followed by the measurement of the ^{14}C radioactivity in the acetate derivatives[65]. These results confirm that each quinone differs from the succeeding homologue of the given group by one isoprene unit (I, n = 6–10). Thus the ubiquinones isolated from natural sources have been characterised as UQ_6 (*Saccharomyces cerevisiae*), UQ_7 (*Torulopsis utilis* A), UQ_8 (*Azotobacter vinelandii*), and UQ_9 (*Torulopsis utilis* B).[28]

III. SYNTHESIS OF UBIQUINONES

1. Synthesis of the Polyisoprenoid Side-Chain

Formula (I) shows that ubiquinones contain an unsaturated side-chain with a variable number of isoprenoid units linked to one another "head to tail". The double bonds in the side-chain have the *trans*-configuration. The corresponding unsaturated terpenoid alcohols [of type (XV), see Scheme 2 and Table 1] with the all-*trans*-configuration of the double bonds, necessary for the synthesis of ubiquinones, were obtained by methods developed in recent years in the chemistry of isoprenoids.

Condensation of acetone (XIII, x = 0) with sodium acetylide in liquid ammonia followed by partial hydrogenation of the product (XIV, x = 0) gives methylbutenol (XV, x = 0).

Scheme 2

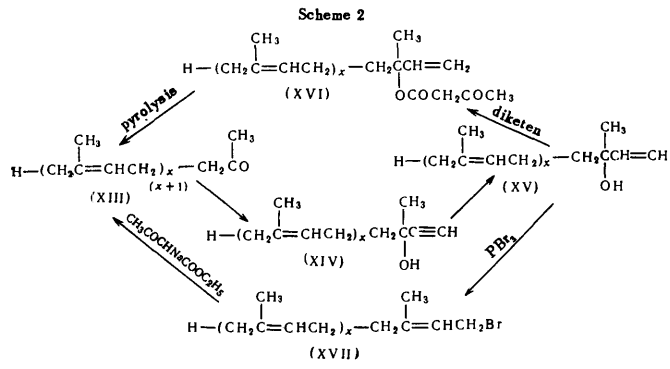


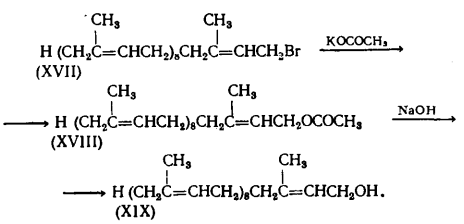
TABLE 1.

x	Ketones	Tertiary alcohols
0	C_5-ketone (A)	C_5-alcohol (methylbutenol)
1	C_8-ketone (methylheptenone)	C_{10}-alcohol (L)
2	C_{13}-ketone (GA)	C_{15}-alcohol (N)
3	C_{18}-ketone (FA)	C_{20}-alcohol (GL)
4	C_{23}-ketone (GGA)	C_{25}-alcohol (FL)
5	C_{28}-ketone (FGA)	C_{30}-alcohol (FN)
6	C_{33}-ketone (FFA)	C_{35}-alcohol (FGL)
7	C_{38}-ketone (FGGA)	C_{40}-alcohol (FFL)
8	C_{43}-ketone (FFGA)	C_{45}-alcohol (FFN) (isosolanesol)
9	C_{48}-ketone (FFFA)	C_{50}-alcohol (FFGL)

A = acetone, G = geranyl, F = farnesyl, L = linalo-ol, N = neralidol.

When the latter is condensed with diketen[66] and the resulting acetoacetate (XVI, $x = 0$) is pyrolysed, methylheptenone (XIII, $x = 1$) is obtained. Repetition of similar operations gives geranylacetone (XIII, $x = 2$) via linalo-ol (XV, $x = 1$); the new double bond in geranylacetone has the *trans*-configuration to the extent of two thirds and the *cis*-configuration to the extent of one third. Subsequent increase of chain length by one isoprenoid unit gives rise to farnesylacetone (XIII, $x = 3$).

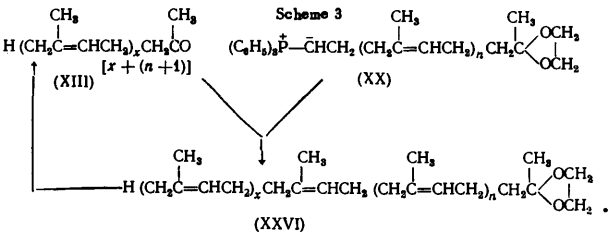
One of the methods of synthesis of isoprenoid ketones consists in the preparation of primary bromides (XVII) from the corresponding tertiary vinyl carbinols (XV) and subsequent condensation with sodioacetoacetic ester[67]. The isoprenoid ketones (XIII) obtained in this way after ketonic hydrolysis contain 85% of the *trans*- and 15% of the *cis*-forms. Subsequent sixfold increments of the chain length of *trans*-geranylacetone (XIII, $x = 2$) by the C_5-unit [68,69] with separation of the stereoisomers gives the *trans*-C_{43}-ketone (XIII, $x = 8$). The latter is converted in the usual way into the primary C_{45}-bromide (XVII, $x = 8$), which is also obtained from the natural alcohol solanesol (XIX).[69,70] This bromide can be converted, via the C_{48}-ketone (XIII, $x = 9$), into the *trans*-tertiary alcohol (XV, $x = 9$) and the corresponding primary C_{50}-alcohol[69]. Treatment of the C_{45}-bromide (XVII, $x = 8$) with potassium acetate followed by hydrolysis of compound (XVIII) gives the C_{45}-alcohol (XIX) which is identical with the natural solanesol, as shown by the determination of the melting point of a mixed sample and a comparison of the corresponding X-ray diffraction patterns[25,69].



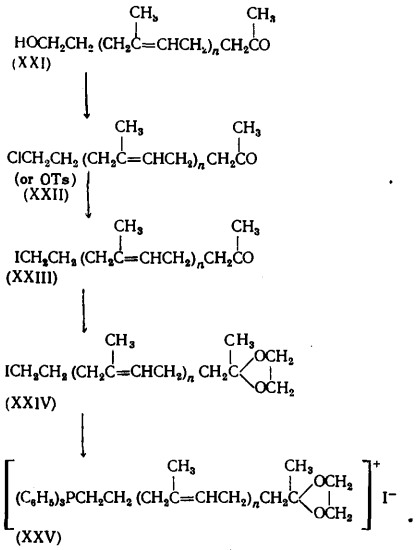
Another method of synthesising polyisoprenoid ketones consists in a gradual increase of the length of the carbon chain by mono-, di-, or tetra-isoprenoid units using difunctional compounds in the Wittig olefin addition reaction[71-73] (Scheme 3).

Isoprenoid ketones of the type of methylheptenone (XIII, $x = 1$), *trans*-geranylacetone (XIII, $x = 2$), and *trans*-farnesylacetone (XIII, $x = 3$) can be made to undergo the olefin addition reaction using the phosphorane (XX).[71-73]

Scheme 3



The bifunctional stereoisomeric phosphoranes (XX, $n = 0$ and $n = 1$) are synthesised from acetylpropanol (XXI, $n = 0$) [71] and the di-isoprenoid C_{10}-keto-alcohol (XXI, $n = 1$) respectively[72,73]: the OH group is replaced by iodine [compound (XXIII)], the carbonyl group is protected by the formation of the ethyleneketal (XXIV), the phosphonium salt (XXV) is formed, and the phosphorane is finally produced by further reaction with sodium methoxide in dimethylformamide:



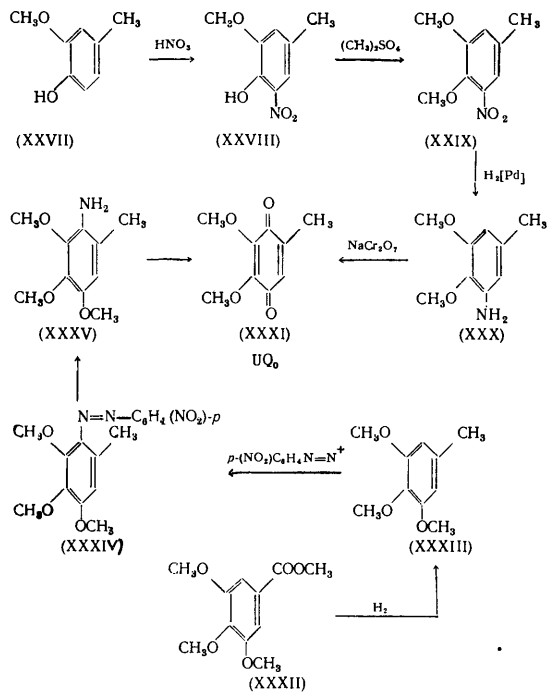
The resulting ethyleneketals (XXVI) with the carbon chain lengthened by five and ten carbon atoms respectively and the isoprenoid ketones (XIII, $x = n + 1$) obtained from them by the hydrolysis of the ketal group are formed as a mixture of *cis*- and *trans*-isomers with respect to the new double bond, in proportions of 60 : 40. Individual *trans*-isomers required for subsequent syntheses are obtained by vacuum fractionation in the case of geranylacetone (XIII, $x = 2$) and farnesylacetone (XIII, $x = 3$). The *trans*-isomers of successive isoprenoid ketone homologues are isolated by crystallisation at low temperatures[65].

2. Synthesis of UQ_0

2,3-Dimethoxy-5-methyl-1,4-benzoquinone (XXXI) — the ubiquinone chromophore — has been called UQ_0 and its position in the series of ubiquinones is analogous to the position of menadione among vitamins K. However, the corresponding biological similarity between UQ_0 and menadione has not been observed[74]. UQ_0 was synthesised long before the discovery of the ubiquinone group[75] (Scheme 4).

Creosol (XXVII), obtained by the reduction of vanillin over $Pd/BaSO_4$ using the Rosenmund method[76], is converted into nitrocreosol (XXVIII),[77] the methylation of which gives 5-nitrohomoveratrol (XXIX). The reduction of the latter to 5-aminohomoveratrol (XXX) and oxidation

Scheme 4



of the amine with sodium dichromate in sulphuric acid yield 2,3-dimethoxy-5-methylbenzoquinone (XXXI).

An alternative synthesis of UQ_0, from the ethyl ester of trimethylgallic acid, was described after the discovery and determination of the structure of ubiquinones[78]. Trimethylgallate (XXXII), obtained by the methylation of gallic acid[79], is reduced over a copper–chromium catalyst to 3,4,5-trimethoxytoluene (XXXVIII). Coupling with *p*-nitrophenyldiazonium salt and subsequent reduction of the diazo-compound (XXXIV) lead to trimethoxytoluidine (XXXV), which is oxidised to 2,3-dimethoxy-5-methylbenzoquinone (XXXI).

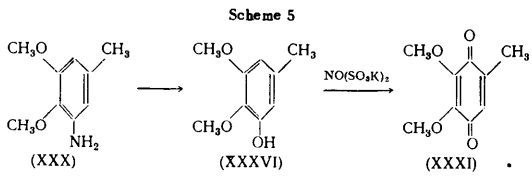
Other syntheses of UQ_0 described in the literature are modifications of the procedures already given above. It has been suggested[80] that 2,3-dimethoxy-5-methylphenol (XXXVI), obtained from aminohomoveratrol (XXX), be oxidised to 2,3-dimethoxy-5-methyl-1,4-benzoquinone (XXXI) with the aid of potassium nitrosodisulphonate (Fremy's salt) (Scheme 5).

In addition UQ_0 (XXXI) can be obtained from nitrovanillin (XXXVII) [8] by the series of conversions shown in Scheme 6.

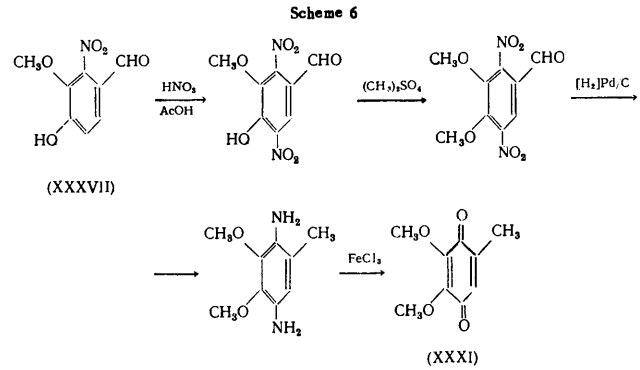
3. Synthesis of UQ_1–UQ_{10}

The ubiquinones UQ_1–UQ_{10} have been synthesised[23,25,67,82–87] by the condensation of 2,3-dimethoxy-5-methylhydroquinone (XXXVIII) with the tertiary (XV) or primary allyl

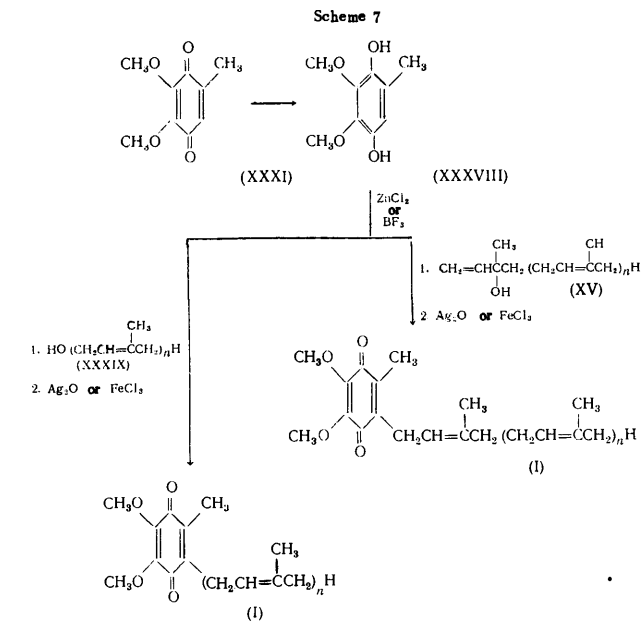
Scheme 5



Scheme 6



Scheme 7



alcohol (XXXIX) to give the corresponding substituted hydroquinones (Scheme 7). Zinc chloride or boron trifluoride-ether or the two together are used as catalysts for this reaction. The hydroquinones are oxidised with silver oxide or ferric chloride to give the ubiquinones (I) (see Table 2).

The identity of the synthetic and natural products has been established by determining the melting points of mixed samples, by ultraviolet and infrared spectroscopy, by paper and thin-layer chromatography, and by X-ray diffraction. The last method proved to be exceptionally accurate for the identification of crystalline isoprenoid homologues[25].

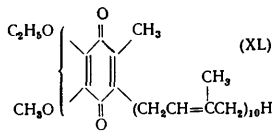
TABLE 2.

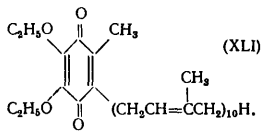
Synthetic quinone	M.p.	λ_{max} = 275 nm in petroleum ether		Synthetic quinone	M.p.	λ_{max} = 275 nm in petroleum ether	
		$E^{1\%}_{1\,cm}$	ϵ			$E^{1\%}_{1\,cm}$	ϵ
UQ_1	oil	590	148×10^3	UQ_6	19—20°	260	153×10^3
UQ_2	oil	455	145×10^3	UQ_7	31—32°	229	151×10^3
UQ_3	oil	390	151×10^3	UQ_8	37—38°	206	150×10^3
UQ_4	oil	326	148×10^3	UQ_9	44—45°	187	149×10^3
UQ_5	oil	292	152×10^3	UQ_{10}	49°	176	152×10^3

IV. CONVERSION PRODUCTS OF UBIQUINONES

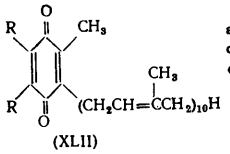
1. Products of the Nucleophilic Replacement of the Methoxy-Groups

The isolation of ubiquinones consists mainly in the hydrolysis of the test substance with hot alcoholic alkali, extraction of the non-hydrolysable lipids, purification of the extracts by column chromatography with the appropriate adsorbent, and crystallisation from polar solvents[32,33]. When ethanol is present in the hydrolytic process, there is a possibility of the nucleophilic replacement of the methoxy--groups, the amounts of the resulting monoethoxy- and diethoxy-derivatives, (XL) and (XLI), depending on the temperature and the duration of hydrolysis[50].


(XL)


(XLI)

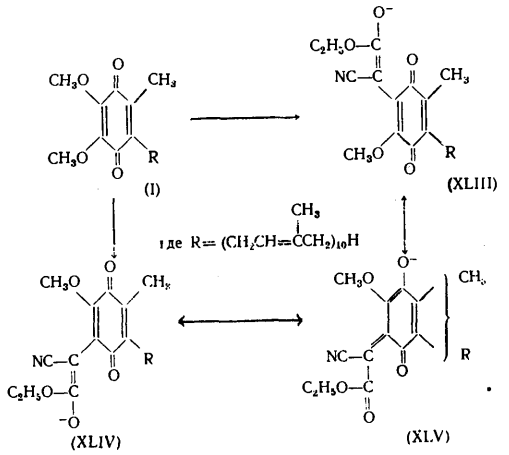
The capacity of the methoxy-groups of the ubiquinones to undergo nucleophilic replacement permits an approach to the synthesis of higher alkoxy-homologues (XLIIa), derivatives containing nitrogen and sulphur [(XLIIb) and (XLIIc) respectively], and the ubiquinone (XLIId) with a radioactive methoxy-group.


(XLII)

a) R=R'O; b) R=R'NH—, R'R"N—;
c) R=R'S—; d) R=$C^{14}H_3O$—;
e) R=$(CH_3)_2CHCH_2CH_2O$—;
f) R=$(CH_3)_2CHO$—.

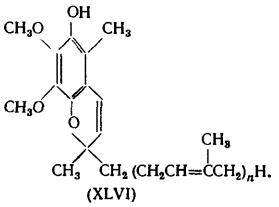
The di-isopentyloxy- and di-isopropoxy-homologues [(XLIIe) and (LXIIf) respectively], which are of definite interest in connection with the determination of the role of UQ_{10} in various enzymic systems, have been synthesised in this way[88].

The determination of UQ_{10} in human urine (a modification of the Craven reaction) is based on this principle[50]. The blue colour produced by the reaction of UQ_{10} with cyanoethyl acetate is due to the conversion of UQ_{10} (I) into compounds (XLIII), XLIV), and (XLV):


(I) (XLIII) (XLIV) (XLV)

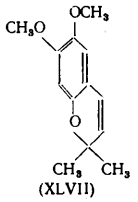
2. Ubichromenols

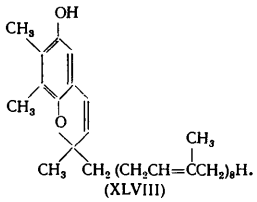
Ubichromenol is the trivial name given to the ubiquinone isomer in which the third carbon atom of the side-chain forms a chromen ring with the quinone oxygen [compound (XLVI)]:


(XLVI)

The nomenclature of ubichromenols is derived from the corresponding ubiquinones. The compound which is the isomer of ubiquinone(50) is called ubichromenol(50) although its side-chain contains only 46 carbon atoms. Ubichromenol(50) (XLVI, n = 9) has been isolated from the kidneys and liver of humans[89] and from the liver of rats suffering from vitamin A deficiency (the substance which was initially denoted by the letters SC [15,34,90-96]).

The structure of ubichromenol(50) was established in a study of its spectroscopic properties[91], by comparing them with those of two known chromens: ageratochromen (XLVII) [97] and solanochromen (XLVIII):[98]


(XLVII)


(XLVIII)

Thus it was shown that ubichromenol(50) (XLVI) is 2,5-dimethyl-7,8-dimethoxy-2-{[3-methyl-2-butenyloctakis--(3-methyl-2-butenylene)]methyl}-3-chromen-6-ol[91].

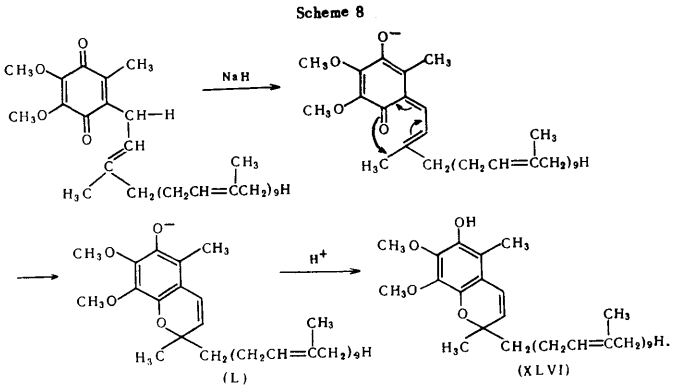
Ubichromenols can be obtained from ubiquinones by passing the latter through an alumina column with subsequent elution using various solvents with[93] and without[94,99] dilute hydrochloric acid. This reaction led to many doubts as to whether ubichromenol as such is a natural component of animal origin or whether it is formed as a result of isomerisation in the organism or during isolation[92,100-103].

Biosynthetic studies using the [2-^{14}C]lactone of mevalonic acid demonstrated convincingly that ubichromenol has a common precursor with ubiquinone and is a product of biosynthesis in the rat organism[104,105]. Furthermore, ubichromenol(50), isolated from human kidneys, is optically active[95,106], while the compound obtained by the cyclisation of UQ_{10} is racemic.

The synthesis of 6-chromenol (XLVI) in high yield has been achieved by the cyclisation of UQ_{10} under the influence of sodium hydride[107] (Scheme 8).

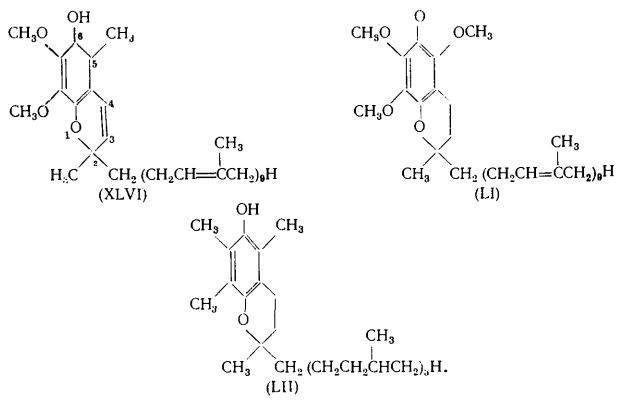
The elimination of a proton from the first carbon atom of the side-chain and the withdrawal of electrons towards the quinone oxygen in position 4 lead in all probability to the intermediate (XLIX) which is stabilised by the electron shift. The formation of the bond between the quinone oxygen in position 1 and the 3-carbon atom in the side-chain yields the 6-hydroxy-anion of 6-chromenol (L). When this intermediate is protonated, ubichromenol(50) (XLVI) is formed.

Scheme 8



Ubichromenols can also be obtained on a preparative scale from ubiquinones in the presence of pyridine [108].

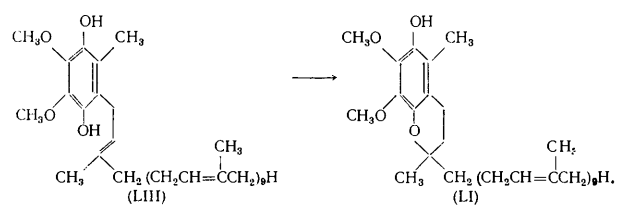
Certain common features in the structure of α-tocopherol (LII) and ubichromenol (XLVI) as well as its analogue saturated with respect to the 3,4-bond [ubichromanol (LI)] led to the investigation of the vitamin activity of these compounds.



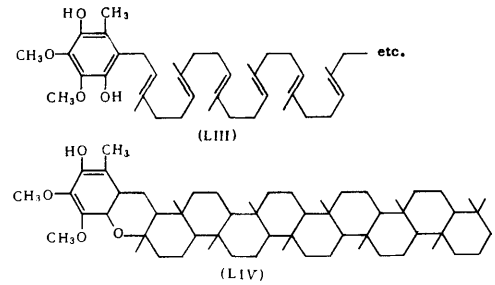
However, it was found [109] that, while ubichromenol exhibits a definite vitamin E activity, ubichromanol (LI), which would appear to be more similar to α-tocopherol (LII), does not. In this connection, ubichromenol may be regarded as a non-specific antioxidant [110,111].

3. Ubichromanols

Interesting observations were made by Folkers in the preparation of the corresponding chromanol (LI) from ubiquinol(50) (LIII): [50]

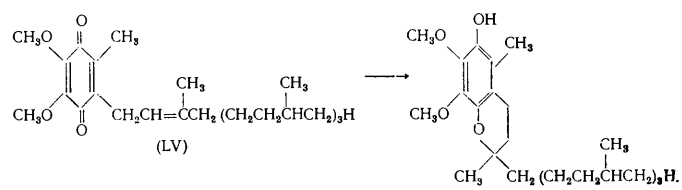


When ubiquinol(50) is treated with potassium bisulphate under conditions which are well known to be suitable for the preparation of 6-chromanols, the corresponding chroman (LI) is formed [112]. However, under the action of stannous chloride [113], instead of the expected product (LI) a mixture of substances was obtained in which, according to NMR spectroscopic data, there are protons characteristic of saturated hydrocarbons instead of the protons characteristic of the isoprenoid chain, and the *p*-hydroxy-group is absent. The authors believe that, as a result of the high reactivity of the isoprenoid side-chain, intramolecular condensation of the isoprenoid residues of compound (LIII) takes place in this case with formation of compound (LIV):



Different degrees of cyclisation of compound (LIII) were responsible for the formation of a mixture of substances.

The formation of the chromanol from hexahydroubiquinone(20) (LV) takes place in the usual way on boiling the quinone in glacial acetic acid in the presence of an excess of stannous chloride:



The double bond of the first, unsaturated isoprenoid unit of the phytol residue of compound (LV) becomes localised on formation of 6-chromanol; there are no other unsaturated centres which would favour the cyclisation of the side-chain of hexahydro-UQ_4. Hexahydroubiquinone(20) is the most convenient member of the ubiquinone group for various biological tests [114].

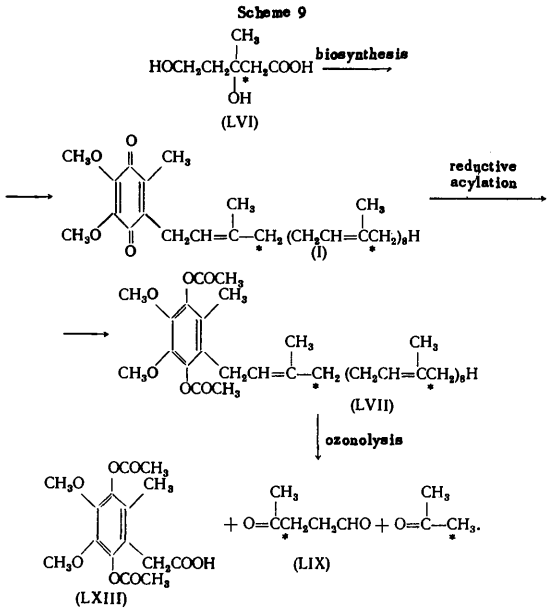
V. BIOSYNTHESIS OF UBIQUINONES

In order to assess the physiological significance of ubiquinones, to which an important function in the oxidative processes in the cell is attributed [115], it is important to know whether the living organism can itself synthesise them or whether they have to be supplied from the outside.

1. Biosynthesis of the Isoprenoid Side-Chain

Experimental studies *in vitro* and *in vivo* showed that [2-^{14}C]mevalonate [104,105,116,117] and [2-^{14}C]acetate [118-121] are incorporated only in the side-chain of the ubiquinone. The limited role of mevalonic acid in the biosynthesis of ubiquinones was confirmed by the oxidative degradation of labelled UQ_9. [122,123] A specimen of [^{14}C]UQ_9, obtained biosynthetically from [2-^{14}C]mevalonic acid (LVI), was acylated reductively to diacetyl[^{14}C]dihydro-UQ_9 (LVII), which was then subjected to selective degradation by ozonolysis. Radioactive levulinic aldehyde (LIX) and acetone were isolated from the reaction mixture as the corresponding dinitrophenylhydrazones (Scheme 9).

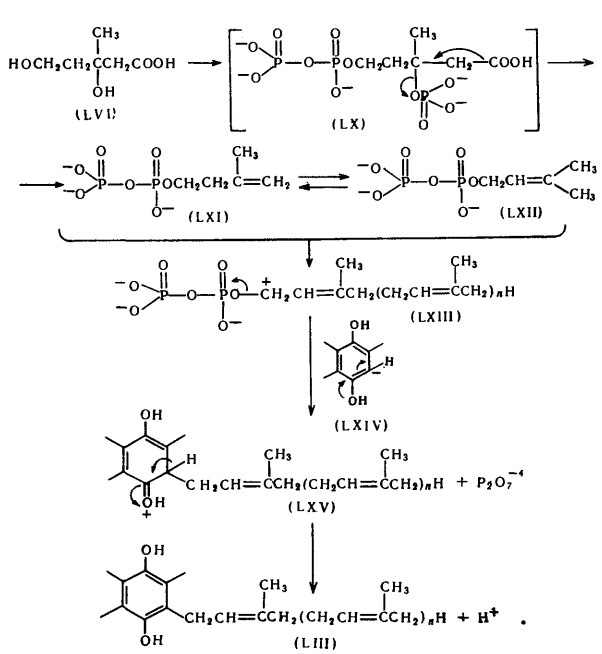
Scheme 9



3,6-Diacetoxy-4,5-dimethoxy-2-methylphenylacetic acid (LVIII), formed from the aromatic ring of the ubiquinone molecule, was isolated in the crystalline form and did not contain the radioactive label.

The above results are consistent with the postulated biosynthesis of terpenoids such as squalene [124] and carotenoids [125], according to which the polyisoprenoid side-chain of ubiquinone can be built up as a result of successive increments by one C_5-unit (Scheme 10). Mevalonic acid (LVI) [126] is converted in three stages into the derivative (LX) with three phosphate residues. As a result of decarboxylation and dephosphorylation, the latter yields isopentenyl pyrophosphate (LXI) [127,128] — "active isoprene" or the "structural C_5 unit" [129]. Δ^3-Isopentenyl pyrophosphate is capable

Scheme 10



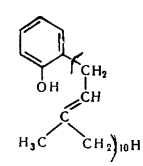
of isomerising to dimethylallyl pyrophosphate (LXII), [128-130] which is the terminal unit in isoprenoid polymers. Successive increments of the chain length of dimethylallyl pyrophosphate by C_5 units leads to isoprenoids with a carbon chain of increasing length, such as geranyl pyrophosphate (LXIII, n = 1), farnesyl pyrophosphate (LXIII, n = 2), etc. Geranylgeranyl pyrophosphate (LXIII, n = 3) [131] and the free alcohol solanesol [132], corresponding to the C_{45}-pyrophosphate (LXIII, n = 8), have been found in animal tissues. These compounds are probably synthesised in the same way as the lower representatives of this group.

Comparatively recently the polymer with twenty isoprenoid residues (C_{100}) has been found in human kidneys and has been given the name dolichol [133,134]. In this connection, one may assume that in the animal organism there are a number of enzymes which are responsible for the formation of polyisoprenoid homologues which are then used for the synthesis of squalene, the side-chains of ubiquinones, vitamins K_2, and other isoprenoids.

2. Biosynthetic Pathways for Ubiquinones

The discovery of allyl pyrophosphate as an alkylating agent in the biosynthesis of polyterpenoids became the basis for the development of a possible mechanism of the addition of the isoprenoid chain to the appropriate hydroquinones [128,129,135,136]. It is suggested that the alkylation of the unknown hydroquinone precursor (LXIV) with allyl pyrophosphate (LXII) involves the formation of an intermediate (LXV), which loses a proton and is converted into ubiquinol (LIII). On the basis of this hypothesis, it is quite likely that in the formation of ubiquinone itself the animal organism can use as donors of aromatic rings certain benzoquinone derivatives supplied with food or synthesised by the intestinal microflora. In this connection, a study has been made of a number of radioactive compounds containing aromatic rings to elucidate their possible participation in the formation of the ubiquinone chromophore. These were aromatic amino-acids [137,138] {[^{14}C]phenylalanine [139-142] and [^{14}C]tyrosin [141]}, vitamin E, [117,143] (labelled with tritium by Wilzbach's method [144]), and also 2,3-dimethoxy-5-methylbenzoquinone, 3-hydroxy-2-methoxy-5-methylbenzoquinone (fumigatin), and 2,3-dihydroxy-5-methylhydroquinone, labelled selectively in position 5. [145] Only [^{14}C]phenylalanine was found to be incorporated into the UQ_9 molecule in rats [146,147].

2-Decaprenylphenol, a biosynthetic precursor of ubiquinone containing simultaneously the aromatic ring and the isoprenoid side-chain, has been isolated recently from the lipid fraction of *Rhodospirillum rubrum* [148], which contradicts the above hypothesis that the incorporation of the isoprenoid side-chain is one of the last stages in the biosynthesis [149].



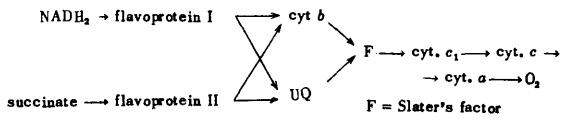
It is believed that this precursor can be obtained by the enzymic decarboxylation of *p*-hydroxybenzoic acid [150,151] after the latter had been first alkylated with decaprenyl pyrophosphate. *p*-Hydroxybenzoic acid is formed biosynthetically from shikimic acid [152].

It has been shown experimentally that, in the biosynthesis of ubiquinone, methionine [149,153] and formate [154] can serve as donors of methyl groups in the *O*-methylation reaction. Furthermore, formate is a source of the methyl group in the benzene ring [154].

VI. ROLE OF UBIQUINONES IN ELECTRON TRANSPORT IN OXIDATIVE PHOSPHORYLATION. HYPOTHESES CONCERNING THE POSSIBLE MECHANISM OF THE PROCESS

Ubiquinones are localised in the mitochondria in animal and higher plant cells at relatively high concentrations (NAD : cyt. $a \simeq$ UQ : cyt. $a \simeq 15$). This suggested that they participate in the electron transport system of the respiratory chain. Experimental data show that, on incubation under anaerobic conditions with substrates such as succinate and $NADH_2$, endogenous ubiquinone in mitochondrial preparations is reduced to ubiquinol while under aerobic conditions the latter is reoxidised to the quinone [155,156] (the redox potential is +0.122 V [157]). Furthermore, the extraction of ubiquinone bound in mitochondria with organic solvents results in loss of enzymic activity, which can be restored by the addition of ubiquinone [158]. In the attempts to determine the function of ubiquinone in electron transport these two findings were the subject of thorough investigations in non-phosphorylating systems [26,158-164]. The results of the determination of the concentration of ubiquinone in mitochondria [165], the kinetics of oxidation–reduction reactions [166-168], and the study of the effect of inhibitors [166] and of the effect of the extraction of ubiquinone on enzymic activity [158,169-174] led to certain hypotheses concerning the role of ubiquinone in the respiratory chain [175].

In the "reconstructed" respiratory chain described by Green [176] in the plenary lecture at the Fifth International Biochemical Congress ubiquinone precedes cytochrome *b*, the entire electron flux passing through ubiquinone. However, later studies in Green's laboratory [177] and Doeg's data [178] showed that ubiquinone and cytochrome *b* provide two alternative pathways for the electron flux [8]:



Comparison of the data on the kinetics of the oxidation–reduction reactions of ubiquinone in mitochondria with the overall rate of electron transport favours the second view [159,166,175,179].

One of the most important achievements of modern biochemistry is the demonstration of the central metabolic role of adenosine triphosphate (ATP) as the universal donor of chemical energy in the cell. The continuous renewal of ATP is an oxidation reaction, in which electron transport is coupled with phosphorylation — with synthesis of ATP. In the animal cell this process is localised in intracellular granules (mitochondria) where all the enzymes required for respiratory phosphorylation and part of the oxidative cell enzymes are to be found. A number of attempts have been made to determine the redox state of ubiquinone in mitochondria as a function of various phosphorylating conditions, in which the effect of inorganic phosphate and ATP was examined [4,168,179-181].

The studies of Todd and coworkers [182] showed that oxidation of quinol phosphates (LXVI) *in vitro* can result in the formation of the "active metaphosphate" (LXVII) which forms pyrophosphate from inorganic phosphate and adenosine diphosphate from adenosine monophosphate (Scheme 11). [183,184]

This scheme constitutes to some extent a model of oxidative phosphorylation. The formation of quinol phosphate from quinone in the presence of inorganic phosphate can be represented by Scheme 12.

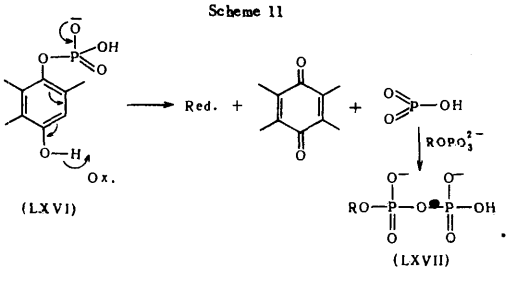
Wieland proposed a simple mechanism for such "reductive phosphorylation" [185] (Scheme 13).

However, many attempts to carry out this reaction with benzo- or naphtho-quinones under various laboratory conditions proved unsuccessful.

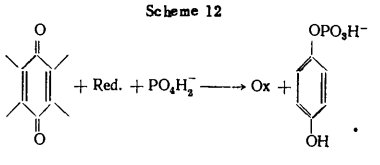
Clark and Todd [186] examined hypothetical ways of obtaining quinol phosphates from quinones in the series of ubiquinones and vitamins K (Scheme 14).

Quinones of type (LXVIII) have a tetrasubstituted quinone ring and a trisubstituted $\beta\gamma$-double bond in the side-chain. The addition of a proton at the β-position leads to a tertiary carbonium ion (LXIX), which is converted into compound (LXX) as a result of nucleophilic attack by the phosphate dianion (HPO_4^{2-}). The reduction of compound

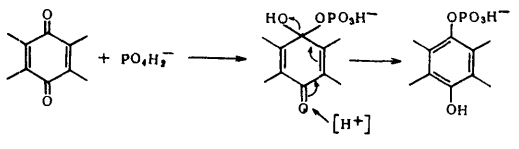
Scheme 11



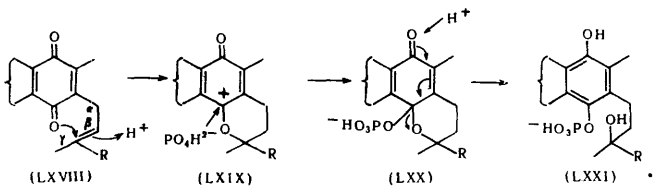
Scheme 12



Scheme 13



Scheme 14



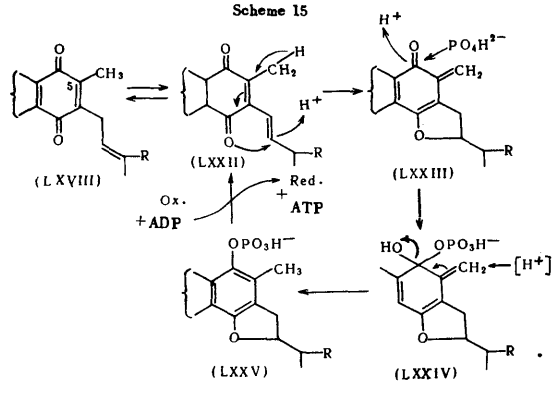
(LXX) and the subsequent opening of the chroman ring result in the formation of the corresponding quinol phosphates (LXXI). It is suggested that compound (LXXI) is then dehydrated and a $\beta\gamma$-double bond forms as in (LXVIII).

The mechanism of the synthesis of quinol phosphates proposed by Todd presupposes the formation of a phosphorus centre in position 4, whereas in biologically active systems this should be located in position 1. The latter was confirmed by a number of workers who demonstrated the phosphorylating role of 6-naphthochromanol phosphate [54,187,188]. Chmielewska [189] noted that ubiquinones and vitamins K with the methyl group in position 5 can occur in an active *ortho*-quinonoid form. The latter exhibits an enhanced capacity for nucleophilic addition reactions. Accordingly, Chmielewska suggested a consecutive series of reactions to account for the participation of quinones in oxidative phosphorylation (Scheme 15).

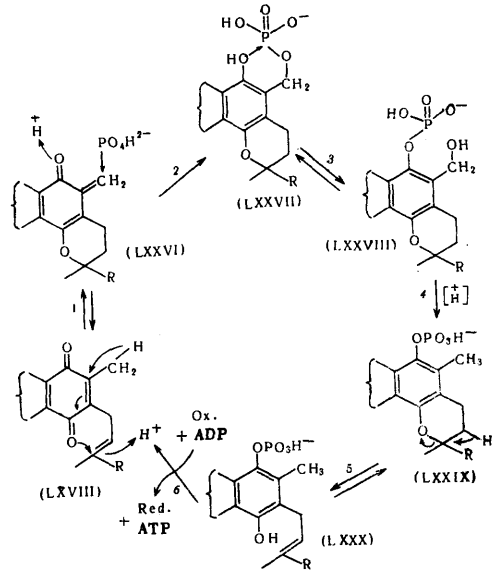
5-Methylquinone (LXVIII) is converted, via the isomerisation product (LXXII), into the *ortho*-quinonoid form (LXXIII), stabilised by the heterocyclic ring. The addition of the phosphate dianion to compound (LXXIII) yields compound (LXXIV), from which the quinol phosphate (LXXV) is then formed. The oxidation of compound (LXXV) is accompanied by the synthesis of ATP and leads to the recovery of the initial quinone, thereby completing the phosphorylation cycle. Chmielewska's hypothesis presupposes the 1,2-addition of the phosphate residue to the quinone oxygen [(LXXIII) → (LXXIV)]. The complexity of the 1,2-addition in such systems renders this mechanism unlikely.

On the basis of purely theoretical considerations, Vilkas and Lederer [190] modified Chmielewska's mechanism and proposed their own version of the mechanism of the addition of inorganic phosphate to methylene quinones (Scheme 16). This scheme presupposes the formation of methylene quinones or quinone methides (LXXVI, reaction 1) with a pyran ring and not a furan ring as suggested by Chmielewska [189], which is confirmed by the existence of chromans in the series of ubiquinones and vitamins K. According to this mechanism the phosphoric acid residue is not fixed at the quinone oxygen but in the 1,4-position of the conjugated quinone methide $O{=}C{-}C{=}CH_2$, with formation of benzyl phosphate (LXXVII, reaction 2). The intramolecular migration of the phosphate residue to the phenolic hydroxyl (LXXVIII, reaction 3) and the reduction of compound (LXXVIII) results in the formation of 6-chromanol phosphate (LXXIX, reaction 4). Ring opening results in the formation of the quinol phosphate (LXXX, reaction 5), which on being oxidised produces ATP and is converted into the initial quinone (LXVIII, reaction 6).

Scheme 15



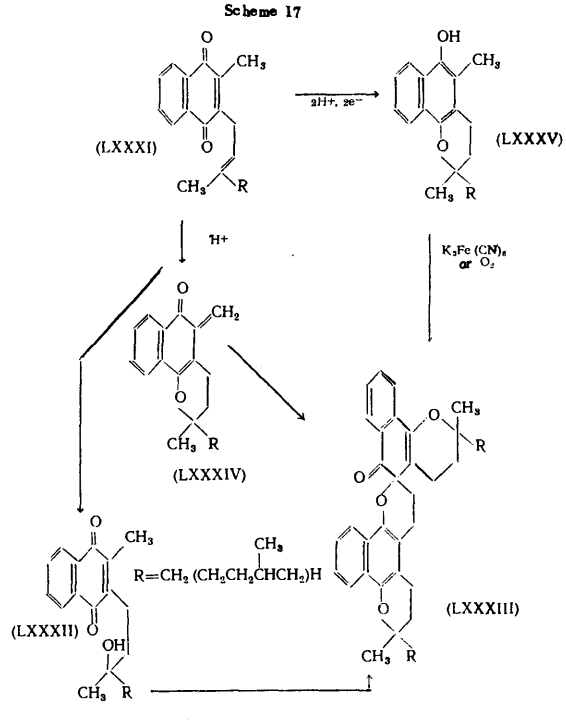
Scheme 16



The key feature of Lederer's theoretical considerations consists in the assumption of the 1,4-addition of the phosphate residue to the quinone methide postulated by Chmielewska. Both authors consider the presence of the methyl group in position 5 of the quinone ring and of the $\beta\gamma$-double bond to be important for the phosphorylation process [191].

In recent years the first two stages of the mechanism, i.e. the formation of quinone methides of chromans (reaction 1) and 1,4-addition to these compounds (reaction 2), have been confirmed experimentally. The studies of Folkers' group [192,193] showed (Scheme 17) that vitamin $K_{1(20)}$ (LXXXI) gives rise to a hydroxyquinone (LXXXII) under the influence of sulphuric acid.

Scheme 17



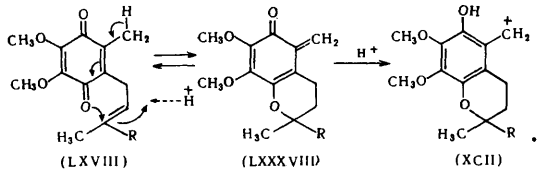
Further reactions in the presence of sulphuric acid gave an oily substance, to which the authors attributed the structure of the dimer (LXXXIII) and showed that the formation of such a compound can be accounted for only by the preliminary formation of the quinone methide (LXXXIV).

Experimental confirmation of the formation of quinone methides was also obtained in Lederer's studies [191,194], in which the dimer (LXXXIII)† was isolated in a crystalline form and its structure was established by mass-spectrometry. It has been shown by means of model reactions that under acid conditions vitamin $K_{1(20)}$ can isomerise to the chromanyl quinone methide (LXXXIV).

Folkers and coworkers [192,193,195,196] obtained 5-phosphomethyl-6-chromanyl acetates (XC, a, b; XCI), the mechanism of the synthesis of which presupposes the intermediate formation of quinone methides and 1,4-addition to the latter (Scheme 18).

When acetyl chloride is allowed to act on γ-hydroxyhexahydro-UQ_4 (LXXXVI), the product is probably the cation (LXXXVII), which is converted via the quinone methide (LXXXVIII) into 5-chloromethyl acetate (LXXXIX). The 1,4-addition is confirmed by the synthesis from compound (LXXXIX) of three new 5-phosphomethyl derivatives (XC, a, b; XCI) [192,196] with the aid of silver dibenzyl phosphate and subsequent selective debenzylation.

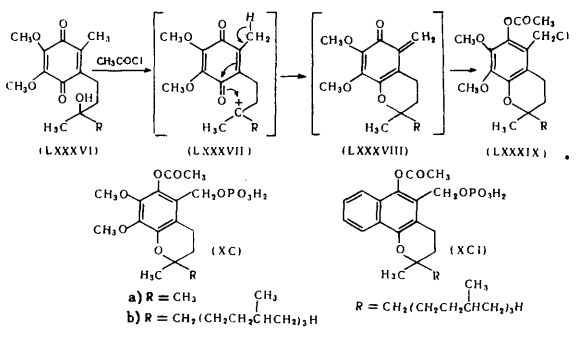
After analysis of the experimental data obtained, Folkers et al. [196] put forward their version of the synthesis of the "active phosphate". The addition of a proton to the double bond of the first isoprenoid unit of the side-chain of compound (LXVIII) results in an electron shift accompanied by cyclisation and the elimination of a proton from the 5-methyl group:



(LXVIII) (LXXXVIII) (XCII)

This is the principal factor in acid catalysed isomerisation. Evidently compounds (LXVIII) and (LXXXVIII) are equivalent in the molecular sense. The addition of a proton to the quinone methide (LXXXVIII) yields the carbonium ion (XCII). The authors believe that this protonated quinone methide (XCII) is a more likely form of quinone methide in chemical reactions in enzymic and non-enzymic processes. The carbonium ion (XCII), which has a deficiency of electrons in the 5-methyl position, is capable of interacting with the phosphate anion. In this connection, the authors suggest the following sequence of reactions, which account for the participation of quinones in oxidative phosphorylation (Scheme 19). Experimental confirmation of this mechanism would render unnecessary the subsequent stages of Lederer's mechanism given above.

Scheme 18



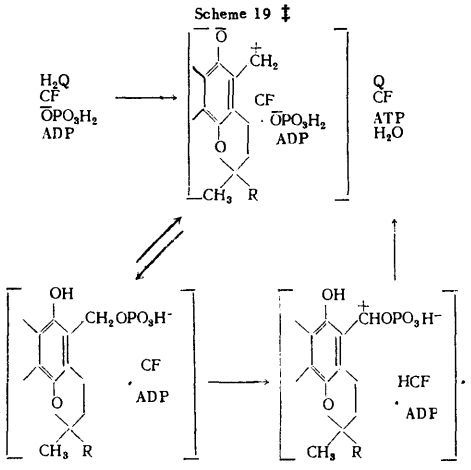
(LXXXVI) (LXXXVII) (LXXXVIII) (LXXXIX)

(XC) (XCI)

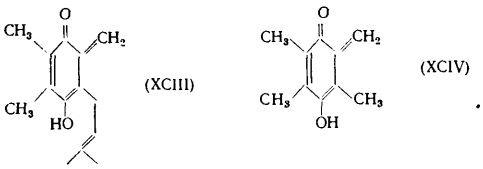
a) R = CH_3 CH_3

b) R = $CH_2(CH_2CH_2CHCH_2)_3H$ $R = CH_2(CH_2CH_2CHCH_2)_3H$

Scheme 19 ‡



Scott put forward a number of new postulates concerning the intermediate compounds in oxidative phosphorylation in the quinone series [197]. On the basis of observations of NMR signals from deuteriated methanol, he suggests the formation of quinone methides without a chroman ring, of the type (XCIII) and (XCIV):



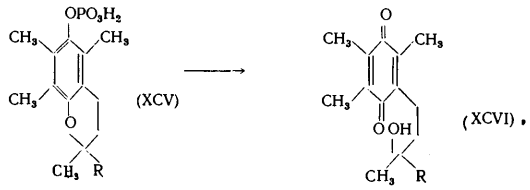
(XCIII) (XCIV)

In Scott's view, such quinone methides are more likely to be in equilibrium with the corresponding quinones than the quinone methides (LXXVI) derived from chromans proposed by Lederer. Furthermore, Scott demonstrated the complexity of the formation of the hydroquinone phosphate (LXXX) from chromanyl phosphate (LXXIX) (Scheme 16) and the reversibility of this reaction, although he does not exclude the probability of a process of this kind in the presence of enzymes. He suggests that direct oxidation of chromanyl phosphate be taken into consideration, and illustrates this using as an example the oxidation of (±)-α-tocopherol phosphate (XCVa) and the phosphate ester

† A dimer of this type can be obtained by oxidising naphthochromanol with potassium hexacyanoferrate(III) [191] or oxygen [233].

‡ CF is the mitochondrial substrate-coupling factor. Scheme 19 is based on the formulae given by R.E.Erickson, A.F.Wagner, and K.Folkers, [J.Amer.Chem.Soc., 85, 1535 (1963)](Ed. of Translation).

of 2,2,5,7,8-pentamethyl-6-chromanol (XCVb) to the corresponding hydroxyquinones (XCVIa, b) in the presence of cerium sulphate.



(XCV) (XCVI),

where R = $C_{16}H_{33}$ (a) and R = CH_3 (b).

The mechanisms quoted above, i.e. hypotheses which explain the chemical reactions of quinones in oxidative phosphorylation, are to a large extent speculative, since none of them has been adequately confirmed experimentally. So far they are working hypotheses, whose validity will have to withstand the test of time.

VII. CERTAIN BIOLOGICAL AND THERAPEUTIC FUNCTIONS OF UBIQUINONES IN ANIMALS AND IN MAN

The role of ubiquinones in intracellular mitochondrial electron transport was considered above.

UQ_{10} has been identified as a component of the liver aldehyde oxidase [198]. This enzyme — which is a xanthine oxidase found only in the homogenate of the soluble fraction of rabbit liver and probably of cytoplasmic origin — has been isolated recently in a crystalline form [198]. The purified enzyme contains two molecules of flavine-adenine dinucleotide, eight iron atoms, two molybdenum atoms, and two UQ_{10} molecules per mole of protein.

The studies of Leonhäuser et al. [199] showed that UQ_{10} is present in microsomes.

The 6-chromanol derived from hexahydroubiquinone(20) has been most widely used in studies designed to elucidate the therapeutic action of compounds of the ubiquinone group in animals and in man. This chromanol facilitates the breeding of rats [114], enhances the mobility of sperm cells in chickens [200], and has a favourable effect on monkey dystrophy [201]. It has yielded satisfactory clinical results in the therapy of certain forms of anaemia in infants [202].

Therapeutic and prophylactic tests recently established that hexahydroubiquinone(20) in the quinone form is active in rabbit dystrophy [203,204]. Furthermore, the study of α-tocopherol deficiency in rhesus monkeys yielded interesting comparative data for UQ_{10} and vitamin E. It was found that UQ_{10} as such markedly increases the number of reticulocytes and the amount of haemoglobin [205]. These are the first data concerning the activity *in vivo* of members of the ubiquinone group in the quinone form.

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During the preparation of the manuscript for the press interesting papers were published on the chemistry of ubiquinones, menaquinones, and tocopherylquinones [206-211,232,233], and yet another natural member of the ubiquinone group, containing 25 carbon atoms in the side-chain (UQ_5) was isolated [212]. Papers were published on the synthesis of the hydroxy-analogues of ubiquinones [213,214] and a definite view concerning the structure of rhodoquinone was established [215].

The discovery of 2-decaprenylphenol [148], the biosynthetic precursor of ubiquinone, and its next analogue 2-decaprenyl-6-methoxyphenol [216], led to a revision of the biosynthesis of ubiquinones. Further studies of this biosynthetic pathway for the cyclic component showed that the ring in ubiquinone, menaquinone, plastoquinone, and α-tocopherylquinone is synthesised from shikimic acid [217-219].

The participation of ubiquinone in electron transport was examined by a number of workers [220-224], and it has been suggested that ubiquinone can have a function other than that of electron carrier [225].

The role of ubiquinones in oxidative phosphorylation was discussed [226,227] and hypotheses have been put forward concerning the impossibility of the participation of ubiquinone methines as intermediates in oxidative phosphorylation [228,229]. Studies on the biological importance of ubiquinones were published [230,231].

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SPECTRA OF ORGANIC MOLECULES IN THE FAR AND VACUUM ULTRAVIOLET

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1. INTRODUCTION

When we study absorption in the visible, the ultraviolet, or the Schumann regions of the spectrum, we are observing a single process: the transfer of electrons to higher energy levels under the influence of light. However, for purely historical reasons, the unnatural classification of electronic spectra by wavelength is still retained. At first, only the visible region was experimentally accessible. Later, when quartz optics and photocells were developed, we became acquainted with the ultraviolet region. Lastly, by using diffraction techniques and LiF and CaF_2 optics, we were able to reach the vacuum ultraviolet region. This is a relatively recent achievement; the technical difficulties still act as a psychological barrier against the widespread application of vacuum ultraviolet spectra in structural problems involving polyatomic molecules. At least two psychological factors militate against the adoption of the vacuum region by chemists. The first is the widespread belief that the necessary techniques are extremely complex and inaccessible. The second, and more important, obstacle is that we know a great deal about the origin of absorption bands in the near ultraviolet and in the visible region, whereas we know practically nothing of the nature of bands in the Schumann region. Thus, the frequent temptation to look beyond the limits of 220 nm is usually demolished by the commonsense question: what shall we learn about this molecule by going further into the short-wavelength region? There are no correlations at all, in this region, between the position and intensity of bands on the one hand and structure on the other hand. Even the spectra themselves are so few that no attempt has been made to classify them systematically.

The aim of the present article is to review the most important results obtained by applying absorption spectra in the far and vacuum ultraviolet to the solution of problems in molecular structure. We hope to convince the reader that the vacuum region is not altogether barren from the chemist's point of view, that the new spectra can be treated as extensions of many existing spectra, and lastly that the techniques involved in recording these spectra have now reached a level comparable to those of the near ultraviolet and infrared region, so that all these regions can now be exploited on an equal footing.

Electronic spectra in the vacuum ultraviolet do not constitute an isolated aspect of theory. To understand these spectra and to make practical use of them, we need a basic knowledge of spectroscopy and of quantum chemistry. Existing textbooks on these subjects are quite good, and deal with the subject at quite different levels. Readers wishing to familiarise themselves with the basic theory are referred to the book by Barrow[1]. A group of three books[2,3,4], read in conjunction, would give a firmer grasp of the subject. Readers approaching spectroscopy from a chemical background will perhaps find the books by Jaffe and Orchin[5] and by Murrell[6] best suited to their needs.

The minimum background knowledge needed to read the present article is the following. We shall assume familiarity on the part of the reader with the form of the complete energy spectrum of a molecule, with the properties of the states giving rise to this spectrum, with possible inter-state transitions, and with the reasons for intensity differences between the observed bands. An appreciation of the origin of the fine structure of electronic bands will be important, as well as the ability to extract from it information on molecular structure. Lastly, it will be necessary to understand some other effects associated with the absorption of light. The review articles by Mason[7] and by Ramsay[8] give a very compact account of all these problems.

The order of presentation of the subject matter will be as follows. We shall first of all discuss the possibility of establishing a relationship between the characteristics of absorption in the far and vacuum ultraviolet and characteristic structural elements. We shall then examine in detail the individual spectra of various classes of organic compounds. Electronic transitions will be designated according to Mulliken's classification[9] and also by the localised orbitals classification[3].

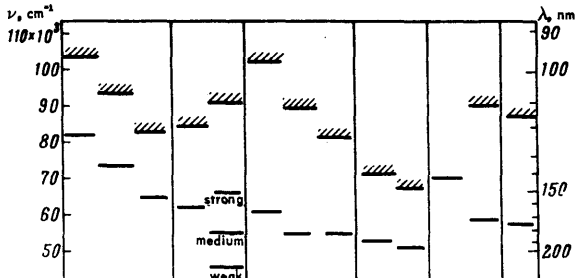
The spectra obtained up to 1944 were classified in the review articles by Sponer[10] and by Platt and Klevens[11]. The fullest account of subsequent work is given by Turner[12]. The books by Phillips[13] and by Rao[14] include a factual summary and a bibliography of vacuum spectra.

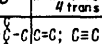
2. CHROMOPHORES IN THE VACUUM ULTRAVIOLET REGION

Electronic spectra are widely used in the study of problems of chemical structure, particularly when chromophoric groups are present in the molecules and characteristic frequencies exist. We shall try to establish whether the concept of a chromophore can in any sense be carried over to the new region. It is immediately apparent that by no means every absorption in the vacuum ultraviolet can be ascribed to the presence of a known chromophore in the molecule. In particular, it is obvious that any organic molecule with saturated bonds absorbs light in this region, whereas not every such molecule contains a chromophoric group in the usual meaning of the word. The term chromophoric is applied to those groups or atoms in a molecule which give rise to absorption by the molecule at the longest wavelengths. The definition is not too loose, since it has been known for a long time that a chromophore does not always produce a colour. We shall retain the term auxochromic for those groups which shift the spectrum towards longer waves. However, a given group can behave either as a chromophore or as an auxochrome in different molecules. For example, in the ethane molecule the C–C bond is a chromophore, and the C–H bonds are auxochromic in the most favourable case. In methane, the C–H bonds are fully chromophoric.

However, this is not merely a matter of terminology. The chromophore concept is a fruitful one if it can be shown that a characteristic absorption is associated with each chromophore. This idea is illustrated in Table 1, which summarises existing information on the longest-wavelength allowed transitions of a series of organic mole-

TABLE 1. Chromophores.



$\log\epsilon_{max}$	4.0	4.0	3.17 2.18 3.40	3.52 3.60		4.2
Oscillator strength, f	0.342		0.046 0.005 0.035		0.0247: w.	
Transition	$\sigma \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$ (trans)	$n \rightarrow \sigma^*$	$n \rightarrow \sigma^*$	$n \rightarrow \sigma^*$; $n \rightarrow \sigma^*$	$\pi \rightarrow \sigma$
Chromophore	C–H; C–C; 	C=C; C≡C			C–F; C–Cl	C=O
Molecule	CH_4; C_2H_6; $C(CH_3)_4$	C_2H_4; C_2H_2	H_2O; CH_3OH; $(CH_3)_2O$	$(CH_3)_2NH$; $(CH_3)_3N$	CF_4; CH_3Cl	H_2CO
References	15; 16; 17; 18	19; 20; 17	21; 21; 22	23; 23	16; 24	7

cules, each of which is the simplest carrier of that chromophore and could therefore stand at the head of a whole family of related compounds. The first impression gained from the Table is definitely unfavourable. Matters improve slightly if the chromophores are classified by transition type: this brings order into the groups in which only one type of long-wavelength transition is possible.

In the paraffin series transitions of the type $\sigma \rightarrow \sigma^*$ only are possible. These transitions occupy the shortest wavelength region. Unsaturated compounds give bands associated with $\pi \rightarrow \pi^*$ transitions, close to the lower absorption edge of the paraffins. All three long-wavelength bands of acetylene are due to these transitions. For oxygen-containing saturated compounds, the transitions of lowest energy will be $n \rightarrow \sigma^*$ transitions. These transitions may turn out to be forbidden (as in methanol), depending on whether the highest filled states taking part in the transition are $2p$ or $2s$. The $n \rightarrow \sigma^*$ transitions localised at an amino nitrogen atom occur at even longer wavelengths. In alkyl halides $n \rightarrow \sigma^*$ transitions are peculiar. They are undoubtedly forbidden, which suggests that an appreciable fraction of $n(2p)$ states takes part in the transition. In ketones, aldehydes, and carboxylic acids, competition of absorption in the long-wavelength region is possible between the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ transitions. Within the limits of Table 1, it is impossible to demonstrate any regularities for these compounds: we shall discuss their spectra in greater detail in the subsequent Sections. At this point, however, it is important to draw attention to the behaviour of the ionisation potentials. They follow the long-wavelength allowed transitions very closely indeed. In some cases the relationship between ν_{max} for the long-wavelength band and the ionisation potential is not merely monotonic, but actually linear.

We shall now turn to the published spectroscopic data, following the classification given in Table 1.

3. THE SPECTRA OF SATURATED HYDROCARBONS

The highest filled orbitals in saturated hydrocarbons are bonding σ-orbitals. In these systems absorption can occur only by transitions of the molecule to the σ^* antibonding state or to Rydberg levels. The simplest member of this series is methane. A knowledge of its spectrum should resolve the problem of the absorption associated with the chromophore C–H in all compounds containing this chromophore. Clearly, we can only talk about the absorption region, since in saturated compounds the electrons are not localised in an individual bond but belong to the whole molecule to an appreciable extent. Figs. 1*a* and 1*b*, taken from the work of Duncan[16] and of Weissler[25], give some idea of the full spectrum of methane. The total oscillator strength, measured by the area between the long-wavelength absorption edge and the onset of ionisation, is 6.1: this is practically the same as the theoretical limit, since the higher molecular orbitals contain just six $2p\sigma$-electrons. This means that all possible transitions for electrons of the valence shell ($N \rightarrow V$ and $N \rightarrow R$ transitions) are concentrated in that interval. From this point of view, the band with a maximum at 1250 Å is due to a $\sigma \rightarrow \sigma^*$ transition, whilst the shorter-wavelength region of the spectrum relates to forbidden Rydberg series converging towards the ionisation potential (12.99 eV).

Unfortunately, the chromophore carrier C–C (ethane) has not been studied in the same detail. We only know[17] that its long-wavelength absorption maximum lies at 1350 Å. This is undoubtedly an $N \rightarrow V$ transition, involving excitation of one of the σ-electrons of the C–C bond to the antibonding σ^* state. Further increase in the number of carbon atoms in the straight-chain alkane series causes the band associated with this transition to shift towards longer wavelengths (Fig. 2). Curve *a* of Fig. 2, based on

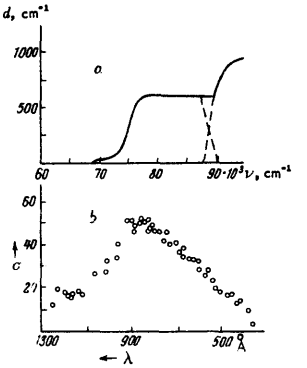


Fig. 1. Absorption spectrum of gaseous methane:
a) absorption coefficients of methane in the region 60 000–95 000 cm^{-1};[16] *b*) absorption cross-sections of methane in the region 1300–500 Å.[25]

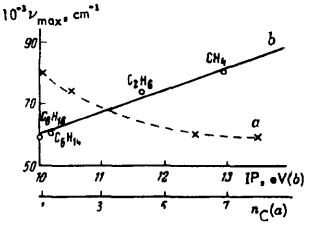


Fig. 2. Relation between the frequency of the long-wavelength absorption maximum of saturated normal hydrocarbons and (*a*) chain length and (*b*) ionisation potential.

experimental data[18,26,27], justifies the conclusion that the wavelength of the absorption maximum for straight-chain alkanes remains practically constant beyond C_6. Despite the scarcity of experimental data, this conclusion seems reasonable, because delocalisation of bonding σ-electrons can extend only over a limited region. Further lengthening of the hydrocarbon chain ceases to affect the distribution of charge among the bonds, and therefore also the absorption spectrum. It is important to remember the linear relationship between ionisation potential and the frequency of the long-wavelength absorption maximum, which suggests that the energy of the highest occupied orbital increases monotonically with the length of the chain. Evidently, when the number of carbon atoms is large enough the energy diagram of the molecule can be described by zones similar to those of a dielectric. Furthermore, branched hydrocarbons absorb at higher wavelengths than their straight-chain isomers[18]. Cyclic hydrocarbons also give spectra at longer wavelengths than the straight-chain linear hydrocarbons, but in this case the wavelengths of the maxima and the oscillator strengths are a function of strain in the ring[28,29]. This is the reason why straight-chain hexane and heptane are often used as solvents in the far ultraviolet. According to Platt and coworkers[30], 0.3 mm layers of these compounds are transparent down to 1705 Å: this is adequate in a large number of cases.

4. HYDROCARBONS CONTAINING DOUBLE AND TRIPLE BONDS

Here we have to deal with two types of $N \rightarrow V$ transition. The first of these originates in exactly the same way as the transition discussed above. The second, on the other hand, is associated with $\pi \rightarrow \pi^*$ excitation. We can predict some of the features of absorption arising from this particular transition on the basis of current ideas. Firstly, this absorption should occur at longer wavelengths, if only because π-bonding is weaker than σ-bonding, and, secondly, the transition should be symmetry allowed.

Let us consider the spectrum of the simplest carrier of the C=C chromophore (ethylene), shown in Fig. 3. The envelope of the fine structure in the region 1400–2000 Å is a very broad band with a maximum at 1620 Å. This is the band which is assigned to an $N \rightarrow V$, $\pi \rightarrow \pi^*$ transition. Studies of its long-wavelength slope[19] revealed a vibrational structure, which becomes diffuse as the dissociation limit (1620 Å) is approached. The absorption showing fine structure, which forms the maximum of the diffuse band and begins at 1750 Å, is caused by an $N \rightarrow R$ transition, where R is the first Rydberg state. The system of doublets denotes transitions to different vibrational levels of this Rydberg state. By using deuteriated materials, Wilkinson and Mulliken[19] were able to show that the long-wavelength components of the doublets correspond to the vibrations of the C=C bond, whereas the short-wavelength components

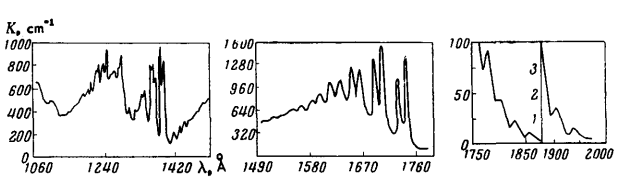


Fig.3. Absorption spectrum of gaseous ethylene[31].

are the even transitions of the oscillations associated with the torsional vibration $\tau_{H-C-H'}$. The higher terms of the Rydberg series lie at 1322, 1247, and 1225 Å, and converge towards the ionisation limit at 10.45 eV, in good agreement with the values of ionisation potential obtained by other methods[26,27].

Let us now return to the $N \rightarrow V$ transition. The long-wavelength side of the band has a vibrational structure whose intensity distribution shows that excitation of the molecule produces an anomalously large increase in the C–C distance: the strongest components of the structure give[19] $\Delta v > 10$. Theoretical analysis[32] of the vibrational structure gives $r_{C-C} = 1.69$ Å as compared with 1.335 Å for the ground state[19]. In the spectrum of tetradeuterioethylene we find, in addition to the stretching vibration bands, bands which can only be ascribed to τ_{H-C-H} vibrations. The difference between the vibrational quantum numbers for these transitions is again very large, which suggests, by the Franck–Condon principle, a very large difference in the angle between the HCH planes in the upper and lower electronic states. This difference is close to 90°. It is difficult to overemphasise the importance of these conclusions. They mean, effectively, that the V-state of ethylene is non-planar. Analysis of many spectroscopic results led Walsh[33] to the conclusion that (1) the planes of the methylene groups are mutually perpendicular; (2) the C–H and C–C bonds form a pyramid at each of the carbon atoms; (3) each carbon atom lies slightly outside the plane passing through the bisector of the H–C–H angle of the opposite methylene group. The first of these conclusions can be readily understood without detailed analysis of the experimental data. Antibonding in the π^*-state is a maximum for the planar configuration of the nuclei, when the carbon $2p$-orbitals are mutually parallel. The repulsion energy will be a minimum, by symmetry considerations, when these orbitals are oriented at right angles to each other. Under these conditions the planes of the methylene groups also will diverge by about 90°. The resulting molecular orbital will no longer be a pure π^*-orbital, and the total bonding will increase to a maximum. Thus, the potential energy of the ethylene molecule, both in the ground and in the excited states, is a periodic function of the angle between the planes of the methylene groups (Fig. 4). The two curves are out of phase by 90°. This means that excitation brings the system into a state of maximum repulsion energy. If the lifetime of the excited

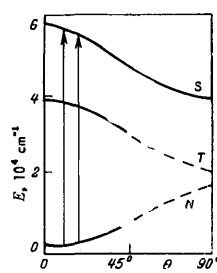


Fig.4. Variation of the potential energy of ethylene with the angle of twist between the planes of the methylene groups for the ground (N), singlet (S), and triplet (T) excited states[7].

state is long enough, the molecule, having dissipated the excess of energy, will be in a state of zero vibrational energy and non-planar nuclear configuration. Such a molecule will behave in a very unusual way in a number of reactions. Equally important is the fact that, when returning to the electronic ground state, the molecule can adopt (with equal probabilities) either the original nuclear configuration or a configuration involving a 180° rotation. With ethylene itself this is immaterial, but if we consider instead *trans*-dichloroethylene, say, we can expect to obtain a new substance, *cis*-dichloroethylene, as a result of this process. The *cis-trans* isomerisation reaction of ethylene derivatives is a very common one. This is evidence that we are indeed dealing with a long-lived excited state, which is a triplet in this case[34]. The Rydberg states correspond to planar nuclear configurations[18], and when a molecule is excited to these states there is no significant change in the shape or in the reactivity of the molecule.

Let us now consider what happens to the $N \rightarrow V$ transition when the ethylene molecule is perturbed in various ways. The introduction of an alkyl substituent into ethylene causes a shift of the band towards longer wavelengths. Longer alkyl substituents give an enhanced shift, but the effect tapers off when the number of carbon atoms in the radical is large (Fig. 5). Similar changes are found in the ionisation potential. Increasing the number of alkyl substituents has exactly the same effect[35-37]. In every case we can envisage a delocalisation of the π-electrons, leading to an increase in the energy of the ground state and a decrease in the energy of the excited state.

A second vinyl or carbonyl group, not conjugated with the first, has practically no effect on the absorption characteristic associated with the $N \rightarrow V$ transition in a C=C double bond[38]. The intensities of non-interacting C=C groups present in the same molecule are additive[39]. All these observations open the way for analytical applications of spectra in the far ultraviolet, at least to alkenes. Table 2 can be used as a key to analytical applications.

Cyclic alkenes are a special group of alkenes. If we compare a linear and a cyclic alkene having the same number of carbon atoms, the cyclic compound is usually found to absorb at shorter wavelengths than the linear compound, the difference increasing with the amount of strain in the ring. The integral intensities or oscillator strengths for the transitions decrease as the strain increases[29,40]. If the molecule contains more than one unsaturated bond, and

TABLE 2. Average position and maximum intensity of the absorption bands (Å) of olefin vapours[39].

Alk-1-enes	1750±25	11800±1200
cis-Alk-2-enes	1765±15	12300±200
trans-Alk-2-enes	1790±10	11700±800
2-Alkylalk-1-enes	1875±15	8900±1200

conjugation between these bonds is established, the spectrum is so strongly shifted towards longer wavelengths that it can appear in the near ultraviolet and thus fall outside the frequency range relevant to the present article. A great deal of relatively recent information on the spectra of unsaturated conjugated systems and of alkenes can be found in Turner's[12] and Mason's[7] reviews, and in the monographs by Rao[14], Murrell[6], and Phillips[13].

The chromophore C≡C is in many ways similar to the previous one. The longest-wavelength transition is again the $N \rightarrow V$ transition from a bonding π-state to an antibonding π^*-state. The electronic structure is still more complicated in this case because the π-states are doubly degenerate. If we choose the Z axis in the direction of the bond, we can consider filled π_x and π_y states, and free antibonding π_x^* and π_y^* orbitals. Ignoring singlet–triplet transitions, we can set up four combinations of these states, but not every one of these can be realised. If the molecule in the excited state is linear, three of the four combinations lead to forbidden transitions and only one can be realised. If, on the other hand, the excited molecule is bent, three allowed transitions are possible, one of which should be relatively weak, by analogy with the corresponding forbidden transition for the case of a linear upper state[41]. This transition should be modified by two types of vibration: by C≡C stretching vibrations and by bending vibrations arising from changes in the H–C–C angle. The spectrum indicates a decrease in the H–C–C angle and an increase in the C–C internuclear distance in the first excited state. Fig. 6 shows the spectrum of gaseous acetylene. Four absorption bands are found in the range 1400–2400 Å. The band with the longest wavelength has a vibrational structure with a red shift, indicating that the internuclear distance increases during excitation. King and Ingold[42] have made a vibrational analysis of the structure. They found evidence for two vibrations: a C≡C stretching vibration with a frequency of 1385 cm^{-1} (as compared with 1974 cm^{-1} in the ground state) and a scissor bending vibration of frequency 1049 cm^{-1} (as compared

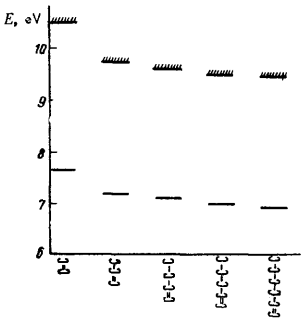


Fig. 5. Relationship between the frequency of the long-wavelength absorption maximum and ionisation potential in the olefin series.

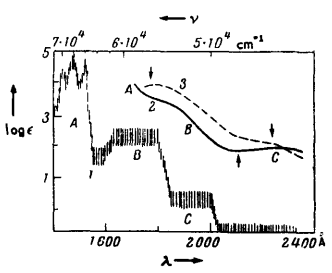


Fig. 6. Absorption spectra[45] of acetylene vapour (curve 1) and of hexane solutions of oct-1-yne (curve 2) and oct-2-yne (curve 3).

with 612 cm^{-1} for the ground state). The transition was found to be polarised at right angles to the plane of the bent molecule, whence it follows that the configuration of the nuclei in this particular excited state has a centre of symmetry. This means that the equilibrium configuration is bent in the *trans* direction. The other two $N \rightarrow V$ transitions correspond to excitation to linear states[43] with an even greater increase in C–C internuclear distance, since the corresponding frequency is lowered to 800 cm^{-1}. Relatively recently Wilkinson carried out a more careful vibrational analysis using deuteriation, and was able to confirm the earlier conclusions[44]. Absorption at wavelengths shorter than 1500 Å is associated with $N \rightarrow R$ transitions. Analysis of this region has shown that the fine structure of the spectrum can be reduced to two Rydberg series converging to a single ionisation limit at about 92 000 cm^{-1}.

Alkylation of acetylene lowers the frequency of all the bands due to $N \rightarrow V$ transitions. At the same time, the intensity of these bands increases. Fig. 6 shows the spectra of two octyne isomers. Bands having the same origin are labelled with the same letter. Other examples have confirmed that alkylation decreases the frequency and increases the intensity. An even stronger red shift and increase in intensity are obtained when hydrogen is replaced by a heteroatom (particularly nitrogen)[46], or by a second $-C{\equiv}CH$ group[47].

The changes occur in the same sense for all bands associated with $N \rightarrow V$ transitions. In the case of heteroatoms, the anomalously large increase in intensity may be due to charge transfer of non-bonding electrons to the free π-orbitals.

The hydrocyanic acid molecule, being isoelectronic with acetylene, should have a similar spectrum: this is confirmed by the work of Herzberg and Innes[48]. However, in this case there are two transitions giving a ben configuration of the molecule: the $\Sigma^+ \rightarrow \Sigma^-$ transition with a band in the region of 1600–2000 Å, and the $\Sigma^+ \rightarrow \Delta$ transition whose absorption lies in the region of 1550–1700 Å.

5. SATURATED COMPOUNDS CONTAINING NITROGEN, OXYGEN, AND HALOGENS

The spectroscopic properties of these compounds are largely determined by the properties of the heteroatoms. The most characteristic feature of their electronic structure is the presence of non-bonding electrons occupying the highest filled levels. We shall consider first the nitrogen compounds.

1. The Chromophore $-\overset{|}{N}-$

We were able to list only five papers on the electronic spectra of aliphatic amines. Yet, these spectra should be a fruitful field of study in short-wave spectroscopy. The simplest carrier of the chromophore is ammonia. Because it has three equivalent N–H σ-bonds and a non-bonding electron pair, ammonia should give rise to a very simple spectrum consisting of one $N \rightarrow Q$ transition, one $N \rightarrow V$ transition at a shorter wavelength than the previous one, and a series of Rydberg transitions. Thompson and Duncan[49] studied the frequency range from 45 000 to 120 000 cm^{-1} and discovered four ammonia bands in this region, which they assigned to Rydberg transitions of the non-bonding pair. Sun and Weissler[25] found a continuum similar to the methane continuum at the short-wavelength end of this range, possibly arising from $N \rightarrow V$ transitions of the electrons localised at the N–H σ-bonds. If this is the case, one of the bands found by Thompson and Duncan[49] should be assigned to the $N \rightarrow Q$ transition. It was recently shown that this interpretation is not definitive: if the four transitions are arranged in a single Rydberg series, the series converges to a potential of 11.58 eV, whereas photoionisation experiments give[50] 10.154 ± 0.01 eV. Vibrational and rotational analysis led Walsh and Warsop[51] to conclude that if the Q-branch frequencies of purely electronic transitions are considered, the Rydberg series including only three transitions (2168, 1434, and 1330 Å) converges towards a reasonable limit (10.1 eV). This is a series of transitions to the 3*s*, 4*s*, and 5*s* atomic states. The other two transitions at 1665 and 1286 Å can be combined into an $n \rightarrow n'p$ series, where n' is the principal quantum number, which takes the values 3 and 4. Vibrational analysis confirmed Walsh's theoretical prediction[52] that ammonia is planar in excited states. The strongest argument is provided by deuteriation experiments. The ratio of the w_{e_2} frequencies for ammonia and ND_3 is the same as the value calculated by the product rule if both molecules have D_{3h} symmetry and the vibration being considered belongs to class A_2''. Another important effect of excitation is an increase in length of the N–H bond. However, in the limiting case involving ionisation of the molecule the N–H bond should be shorter than in the ground state of the neutral molecule because the electron repulsion energy is decreased. Since we expect these changes to be continuous, we may think that, as the excitation energy increases in the sequence 3*s*, 4*s*, 5*s*.... NH_3, the bond length increases more and more slowly and eventually starts to decrease. All this is difficult to reconcile with identity of configuration in all excited states, including the ground state of the $\overset{+}{N}H_3$ ion†. The increase in length of the N–H bond was confirmed for the first excited state by Douglas[54] on the basis of an analysis of the rotational structure (1.08 Å as against 1.01 Å in the ground state). Douglas also showed that practically all electronic transitions in ammonia show signs of predissociation, and we must therefore assume strong interaction between singlet and unstable triplet states. It would appear that, somehow, there is no room for the $N \rightarrow Q$ transition in the range we are discussing. It is possible, however, that this transition falls into the long-wavelength region with alkylated ammonias.

Förster and Jungers[55] recorded the spectrum of methylamine and its deuterium derivatives in the region 2500–2000 Å. They observed a single electronic transition in this region, with a resolved vibrational structure, which can be described by the formulae

$$\begin{aligned}
CH_3NH_2 \quad & \nu = 41\,680 + v_1 \times 650 + 1000 \ cm^{-1} \\
CD_3NH_2 \quad & \nu = 41\,780 + v_1 \times 600 + 870 \ cm^{-1} \\
CH_3ND_2 \quad & \nu = 42\,540 + v_1 \times 515 + 1000 \ cm^{-1} \\
CD_3ND_2 \quad & \nu = 42\,580 + v_1 \times 500 + 825 \ cm^{-1}.
\end{aligned}$$

Thus, the electronic transition giving rise to the band at the highest wavelength is modified by two vibrational frequencies. One of these is strongly affected by deuteriation at the nitrogen atom, the other by deuteriation at the carbon atom. This allows us to ascribe the frequency 650 cm^{-1} to

† See also Duncan's comments[53] in connection with the force constants of the bending vibrations of the planar and the pyramidal structure.

scissor bending vibrations of the N–H bond, and 1000 cm^{-1} to vibration of the methyl group. The corresponding frequencies in the ground state are 783 and 1127 cm^{-1}. Since no other frequencies appear in the vibrational structure, we are dealing with an $N \rightarrow R$ transition of non-bonding electrons to the nearest Rydberg state.

It would nevertheless be very surprising if no room were found for the $N \rightarrow Q$ transition among the long-wavelength transitions in alkylamines: the transition should be strong, since the transition moment in this case is large[56].

Tannenbaum and coworkers[23] have systematised the spectroscopic data on alkylamines (see Fig. 7). They found three broad overlapping bands in the range 45 000–65 000 cm^{-1}. The maximum of the band at the shortest wavelength lies outside the above limits with primary and secondary amines, and can be seen only in tertiary amines. The long-wavelength band, on the other hand, is visible only in primary amines: it strongly overlaps the middle band in secondary amines and is quite invisible in tertiary amines because of the intense middle band. Table 3 gives a fuller account of the influence of structure on the spectroscopic characteristics of an amine.

It can be seen from Table 3 that the long-wavelength band is not markedly affected by substitution. This confirms the suggestion that the long-wavelength transition is the first Rydberg transition of non-bonding electrons of the nitrogen atom to the 3s atomic state of nitrogen. The second transition in the amine series is sensitive to substitution, and can therefore be interpreted as an $N \rightarrow Q$ transition of the non-bonding electrons to the antibonding σ^*-orbital. The decrease in frequency of the second band maximum and the sharp increase in intensity upon alkylation suggest that in this case the n-electrons are excited to antibonding orbitals localised mainly at C–N bonds. Thus, as far as the second transition is concerned, we can envisage charge transfer of n-electrons, leading to a decrease in binding energy and dipole moment in the excited state of alkylamines.

There is another way of testing whether these bands have been correctly assigned to n-electron transitions. When alkylamines are dissolved in acids, the proton of the acid is taken up by the nitrogen, forming a salt and binding the n-electrons. Under these conditions, absorption in the region under discussion vanishes completely[23]. Dissolution of alkylamines in water or alcohols causes a characteristic short-wavelength shift in both bands, resulting from the formation of a hydrogen bond which lowers the energy of the n-electrons.

The relationship between the spectroscopic characteristics of alkylamines and the basicity of the nitrogen atom is particularly important. Fig. 8 shows the n-electron levels in the two lowest unoccupied orbitals relative to the first ionisation energy, taken as $E = 0$. It is evident that the energy of the n-electrons increases with alkylation. This is accompanied by a decrease of the frequency of maximum absorption for the $n \rightarrow \sigma^*_{C-N}$ transition. It is natural to assume that the basicity of the nitrogen increases in this series. Measurements of the ionisation constant confirm that the basicity increases from ammonia to secondary amines, but the measured basicity of tetriary amines turns out to be anomalously low. It is believed that the increase in basicity is cancelled out by steric hindrance to proton addition. Hence it is reasonable to distinguish intrinsic basicity, resulting from the electronic structure of the molecule, from the realisable basicity, which is determined by the steric factors of the reaction as well as by the electronic structure. It is obvious that the spectroscopic characteristics of an isolated molecule should correlate with the intrinsic basicity. This may be the reason for the lack of reasonable correspondence between the pK_B values and the spectroscopic characteristics of cyclic

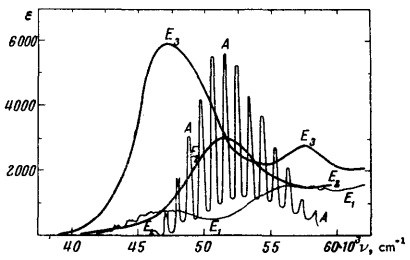


Fig. 7. Absorption spectra of gaseous ammonia (A), ethylamine (E_1), diethylamine (E_2), and triethylamine (E_3)[23].

TABLE 3. Positions of band maxima and transition intensities in amines.

	Ammonia	Methylamine	Dimethylamine	Trimethylamine	Ethylamine	Diethylamine	Triethylamine
First band							
max. position, cm^{-1}	51500	46500	45000	44000	47000	(45000)	—
ϵ_{max}	5600	600	(100)	900	800	(300)	—
f	0.079	0.017	0.0017	0.016	0.019	(0.0028)	—
Frequency of 0–0 transition	46140	41690	—	—	42870	—	—
Second band							
Max. position, cm^{-1}	66000	57500	52500	50250	56500	51500	47250
ϵ_{max}	—	2200	3300	3950	1600	3000	(5900)
f	0.0095	0.084	0.10	0.13	0.050	0.10	(0.18)
Frequency of 0–0 transition	60135	(50360)	45870	—	—	—	—
Difference between maximum frequencies of first and second band, cm^{-1}	14500	11000	7500	6250	9500	6500	—

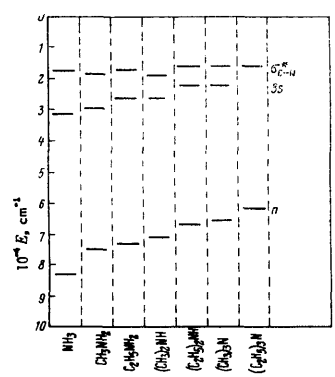


Fig. 8. Ground and nearest excited states of various aliphatic amines[23,26,27].

amines[57]. We should consider yet another factor which may limit the realisable basicity. The non-bonding electron pair of the nitrogen in amines occupies a hybrid orbital, formed by the superposition of s- and p-atomic orbitals. If the s-character is predominant, the resulting orbital is localised close to the nucleus and therefore resides within the van der Waals sphere of the atom. In the opposite limit, when the n-electrons are effectively in a pure p_Z state (e.g. in the pyridine molecule), the electron density distribution is more diffuse and part of the electron cloud can extend beyond the van der Waals sphere. However, the most directional orbital of the carbon atom will be an sp^3-hybrid bonding orbital. This maximises the probability of direct contact between the interacting species — the first step in the process of proton addition. In this sense, the hybrid strength or the value of the homopolar dipole moment is an important characteristic of the basicity[3]. Thus, we can say that the basicity of an amine should increase as the ionisation potential decreases and as the homopolar dipole increases. Information on the homopolar dipole may possibly be obtained by analysing the intensities of the $n \rightarrow \sigma^*_{C-N}$ transitions in different amines, assuming that the orbital of the n-electrons can be approximated by the combination $a2s + b2p$ and estimating the ratio a/b. In general, the intensity of $n \rightarrow \sigma^*$ transitions is surprisingly sensitive to structural changes. For example, axial or equatorial methyl groups at C_2 in cyclic amines cause absorption at practically the same frequencies, but the maximum intensities of the corresponding bands differ by a factor of three or four[58]. These anomalous changes in intensity suggest the presence of some specific intramolecular interactions (between the methyl group and n-electrons) which only an equatorial methyl group can undergo. Changes in ring strain also give rise to remarkable changes in band intensity. The oscillator strength for the $n \rightarrow \sigma^*_{C-N}$ transition[57] is 0.11 for piperidine and 0.05 for pyrrolidine. The intensities fall off appreciably when amines are dissolved in polar solvents, the effect increasing with the polarity of the solvent[57,58]. The bands also suffer a short-wavelength shift, which can be taken to indicate that n-electrons are involved in the transition.

The great sensitivity of the spectroscopic characteristics of amines towards structural changes in the molecules and towards the properties of the medium justifies our hope that spectroscopic studies will soon become a standard method of investigating this large and important class of compounds.

In conclusion we note that the tendency to form planar configurations in the excited state should persist in alkylamines. This cannot fail to have a significant effect, particularly in the isomerisation of cyclic amines, alkylation, and above all in the preparation of amides.

2. The Chromophore -O-

The chromophore -O- is common to water, alcohols, and ethers, but the attention given to these compounds by research workers has differed widely. About 90% of the papers on the electronic spectra of oxygen-containing saturated compounds relate to water. The remaining 10% are shared between ethylene oxide and all other alcohols and ethers. This state of affairs is quite reasonable, since water, being the simplest of all carriers of the chromophore, is the natural touchstone of theory. A preliminary idea of the absorption spectrum of water can be obtained by considering, in Mulliken's approximation, the molecular orbitals of the ground and of the lowest excited state. According to Mulliken[59,60], the ground state of the H_2O molecule, ignoring the $(1s)^2$ electrons, can be represented as follows:

Orbitals	$(2sa_1)^2$	$(yb_2)^2$	$(za_1)^2$	$(2xb_1)^2$	$^1A_1$
Localisation	O	HOH	HOH	O	
Ionisation potential, (eV)	32	18	17	12.7	

The second line shows the atom or group at which the state orbital is localised. The third line gives the energy of these orbitals or ionisation potential calculated in the zeroth approximation (except for the last). Thus, the highest orbital is the orbital of non-bonding $(2xb_1)^2$ electrons, which are localised mostly at the oxygen atom. The nearest excited state can be obtained from the ground state by moving one of the electrons $(2x)$ to the first Rydberg $3s$ atomic orbital of the oxygen, leading to the state $(2sa_1)^2(yb_2)^2(za_1)^2(2xb_1)(3sa_1)$. This state can be a triplet $^3A_1$ or a singlet $^1A_1$. The band observed[21] at 1667 Å can be assigned to a transition of the molecule to this state. The anomalously large width of this band is ascribed to predissociation, leading to $O + H_2$ $(^1\Sigma^+_g)$[59], but an alternative interpretation is possible[61]. The region below 1250 Å shows a series of absorption bands: these can be combined in a Rydberg series, whose members have a vibrational and rotational structure. By analysing the fine structure for H_2O and D_2O, Bell[61] was able to estimate the changes in bond length and bond angle accompanying excitation. Absorption at 1240 Å lengthens the O–H bond by 0.065 Å and increases the angle by 5.2°. The corresponding value for the band system at 1219 Å is 0.067 Å. Bell's analysis also shows that the oxygen n-electrons are bonding, whilst the 3s and 3p atomic orbitals are to some extent antibonding in the water molecule. Bell considers this to be the cause of the continuum at 1655 Å.

In the alkyl derivatives of water only the long-wavelength transition can be associated with the oxygen atom. Alkylation brings about several interesting changes. Replacement of hydrogen by methyl lowers the transition frequency by 5500 cm^{-1} and decreases the intensity by an order of magnitude. Increasing the length of the radical by one unit raises the intensity but has little effect on the frequency. Further increase in the length of the radical lowers the intensity again, but for a secondary alcohol with the same number of carbon atoms the intensity is higher. These changes are summarised in Table 4.

The intensity of this band begins to increase with chain length[30] in the spectra of alcohols with still longer straight-chain hydrocarbon radicals.

Replacement of hydroxylic hydrogen by an alkyl group causes a sharp increase in the intensity of the long-wavelength transition. Also, this transition is accompanied by

TABLE 4.[21]

Substance	Frequency, cm^{-1}	ϵ	f	Ionisation potential, eV
Water	60000	1480	0.0460	12.59
Methanol	54500	150	0.005	10.86
Ethanol	55100	320	0.008	10.50
1-Propanol	54600	240	0.006	10.15
2-Propanol	55300	620	0.015	10.09

a clear vibrational structure in the spectra of ethers. Methyl ether and ethyl ether show this behaviour most clearly (Fig. 9)[62]. The first band has structure with spacing of about 400 cm^{-1}, which can be ascribed to C–O–C bending vibrations in the excited state. The structure of the second band of methyl ether includes the frequencies 2100 and 1300 cm^{-1}, corresponding apparently to stretching and bending vibrations of the methyl group[22,62]. This means that the second band is generated by a transition to antibonding levels of the alkyl substituents, and not to oxygen atomic levels. The spectrum of ethylene oxide[63] is strongly displaced towards short wavelengths as compared with non-cyclic ethers. The bands of 1,3-dioxan occur at shorter wavelengths than those of 1,4-dioxan[64]. This allows us to conclude that in 1,3-dioxan the two oxygen atoms are independent. Another interesting observation is that absorption in 1,4-dioxan is stronger than in tetrahydropyran, but not by a factor of two, as would have been expected if the oxygen atoms had been independent (see Fig. 10). A vibrational band structure observed in cyclic ethers can be assigned to deformation of the ring

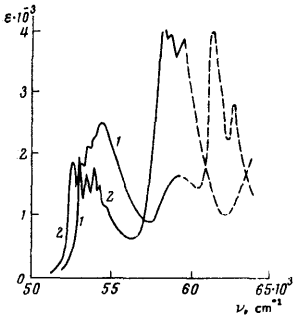


Fig. 9. Absorption spectra of gaseous ethyl ether (curve 1) and methyl ether (curve 2)[62].

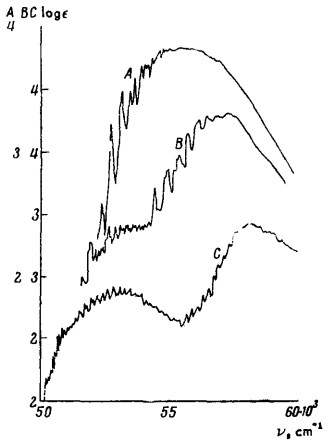


Fig. 10. Absorption spectra of gaseous 1,4-dioxan (*A*), tetrahydropyridine (*B*), and tetrahydrofuran (*C*)[65].

(frequencies in the region of 200 cm^{-1})[65,66]. The absence of one of the bands from the dioxan spectrum is ascribed to the higher symmetry of this compound. Furthermore, because of the presence of a centre of symmetry, the electronic band of 1,4-dioxan cannot show out-of-plane vibrations. The whole of the experimental data on the vacuum spectra of alcohols and ethers suggests that the long-wavelength bands are due to a transition involving non-bonding electrons. The $N \rightarrow V$ transitions in these compounds are concentrated in the region 500–1300 Å, and are weakly perturbed by the proximity of the hydrocarbon part of the molecule to the oxygen atom. In particular, the absorption by methyl, ethyl, n-propyl, and n-butyl alcohols has a maximum at 800 Å, and the intensity ratio of the bands is in strict proportion to the ratio of the number of C–H bonds (3 : 5 : 7 : 9), with a slight discrepancy in the case of n-propyl alcohol[67].

The identification of $n \rightarrow 3s$ and $n \rightarrow \sigma^*$ transitions is a controversial problem in saturated oxygen-containing compounds, as it is in aliphatic amines. This is because the first term of the Rydberg series is not described as a rule (see, for example, Walsh and Warsop[51]) by the Rydberg formula, and therefore the position of the first transition cannot be determined rigorously. The $n \rightarrow \sigma^*$ transition also is to be expected in the long-wavelength part of the spectrum.

Tsubomura[56] and others consider that the absorption spectra of water, alcohols, and ethers can be given a unified interpretation by postulating that: (1) the long-wavelength band is due to an $n \rightarrow \sigma^*$ transition where the n-orbital is a pure $2p$ atomic orbital of oxygen; (2) σ^*_{C-O} lies below σ^*_{H-O}; (3) the matrix element of the Hamiltonian for the σ^*-orbitals is small. If these assumptions are correct — and several arguments can be put forward in favour of the last two — the orbitals σ^*_{C-O} and σ^*_{O-H} in these spectra are non-interacting, but the σ^*-orbitals in water and in the ethers interact strongly owing to degeneracy. This explains why the first transition occurs at longer wavelengths in the ethers than in the alcohols. Calculation of the oscillator strengths for water, alcohols, and ethers, based on the same postulates, leads the authors to conclude that the values should decrease in the sequence water, ethyl ether, ethanol. The observed values are 0.084, 0.041, and 0.013 respectively. The qualitative agreement between calculation and experiment indirectly confirms the validity of the assumptions (including the first). Thus there are arguments in favour of both the $N \rightarrow Q$ and the $N \rightarrow R$ [62] interpretation of the long-wavelength transition. There can be no doubt, however, that the nature of this transition is molecular rather than atomic, since its characteristics are strongly dependent on the nature of the substituent groups. Thus it is meaningful to envisage some composite molecular orbital as the upper state of the first transition.

3. The Halogen Atom Chromophore

The electronic structure of the C–Hal bonds is very similar to that of the C–O bond. However, the observed absorption may lie in the far ultraviolet (70 000 cm^{-1} for CF_4 [20]) as well as in the near ultraviolet (40 000 cm^{-1} for CH_3I [7]). This absorption is due to transitions from n-electron levels. As in the case of alcohols, the intensity is low (see Table 5). The long-wavelength transition can be interpreted as an $n \rightarrow \sigma^*$ transition with the same justification as in the case of the oxygen-containing compounds.

TABLE 5.

Substance	λ, Å	ε	f	References
CF_4	1250	—	0.024	19
CCl_4	1740	2500	0.063	56
$CHCl_3$	1755	1000	0.026	56
CH_2Cl_2	1790	510	—	56
CH_3Cl	1690	370	0.01	56
CH_3Br	2040	200	—	7
CHI_3	3490	230	—	7
CH_2I_2	2915	1320	—	7
CH_3I	2575	365	—	7

TABLE 6.

λ_{max}, Å	Oscillator strength	Assignment		
		transition	symmetry of upper state	selection rules
1700	0.5	$\pi \rightarrow \pi^*$	$^1A_1$	allowed
1800	0.02	$n \rightarrow \sigma^*$	$^1B_2$	allowed
2800	0.0004	$n \rightarrow \pi^*$	$^1A_2$	forbidden by symmetry
3500	10^{-5}	$n \rightarrow \pi^*$	$^3A_2$	forbidden by symmetry and multiplicity

6. COMPLEX CHROMOPHORES

We have so far considered only chromophores which absorb in the far and vacuum ultraviolet. In this sense, the chromophores were simple ones. We shall now discuss the short-wavelength absorption of the familiar chromophores, which we shall term complex because they absorb both in the near and in the far ultraviolet. The simplest of these is the carbonyl group in saturated systems.

The C=O Chromophore

The simplest carrier of this chromophore is formaldehyde, whose ground state can be described as

$$[(1s_C)^2(1s_O)^2(2s_O)^2(\sigma_{CH})^2(\sigma_{CH})^2(\sigma_{CO})^2(\pi_{CO})^2(n_O)^2]\,A_1.$$

Transitions to the following excited states are possible:

$$\ldots(\pi_{CO})^2(n_O)(\pi^*),\quad A_2$$
$$\ldots(\pi_{CO})(n_O^2)(\pi^*),\quad B_1$$
$$\ldots(\pi_{CO})^2(n_O)(\sigma^*).\quad B_2$$

These transitions give rise to absorption bands at relatively long wavelengths. The next transition (towards shorter wavelengths) may be due to excitation of an electron from one of the bonding σ-levels, either σ_{CH} or σ_{CO}. An analysis of the symmetry of the initial and of the final state is needed to establish which of these transitions actually occurs, and with what intensity. Remembering that the formaldehyde molecule has C_{2v} symmetry, we can ascribe a definite symmetry also to the electronic configurations of the various states, which gives us a basis for applying the selection rules. These rules tell us that the $A_1 \rightarrow A_2$ transition is forbidden by symmetry, since all three components of the dipole moment of the transition are equal to zero, whilst the $A_1 \rightarrow B_1$ and $A_2 \rightarrow B_2$ transitions are allowed. If we allow also for spin conservation, the $^1A_1 \rightarrow {}^3A_2$ transition must have the lowest intensity, because the spin of the electron changes. Table 6 [1] lists the approximate positions of typical absorption bands for formaldehyde and symmetrical ketones, the oscillator strengths, and assignments of the bands to the appropriate transitions.

Formaldehyde, in particular, has the following set of absorption bands[7]: 3100 Å (ε = 5), 1749 Å (ε = 18 000), and 1555 Å (ε = 23 000). Their assignment presents no difficulty if we remember that none of these bands are caused by singlet–triplet transitions. With other symmetrical ketones, however, the situation may be more complicated, and further investigation is needed to distinguish $N \rightarrow Q$ and $N \rightarrow V$ transitions. In this respect, a characteristic property of the transitions, such as the shift in the maximum absorption frequency on going from the gas to a solution, can be of considerable help, if the ketone molecules become solvated by molecules of the solvent. Under these conditions the $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands are shifted towards shorter wavelengths, whilst the $\pi \rightarrow \pi^*$ band moves towards longer wavelengths[14,68].

Let us return to formaldehyde. The band at 1749 Å is diffuse, possibly as a result of predissociation. This band is fairly confidently assigned[69,70] to the $n \rightarrow \sigma^*$ transition. The band at 1555 Å has a clear vibrational structure whose spacing (1250 cm^{-1}) is probably related to stretching vibrations of the C=O group in the excited state[69]. This band is confidently assigned[70] to a $\pi \rightarrow \pi^*$ transition. Rydberg absorption begins at 1397 Å. The two series which are observed converge to an ionisation potential of 10.83 ± 0.01 eV.

Alkyl substituents shift the $n \rightarrow \sigma^*$ transition towards longer wavelengths (1749 Å for formaldehyde, 1816 Å for acetaldehyde, 1950 Å for acetone)[7]. The $\pi \rightarrow \pi^*$ transition does not show a definite trend (1555 Å for formaldehyde, 1650 Å for acetaldehyde, 1540 Å for acetone). The ionisation potential rises continuously with alkylation and with the length of the alkyl chain.

Acetone and other aliphatic ketones show yet another band in the 1500–1700 Å region, whose assignment raises special difficulties. Its intensity increases with the degree of branching at the α carbon atom[71,72], whilst at the same time the band shifts towards longer wavelengths. Holdsworth and Duncan[71] analysed the behaviour of this band, and concluded that a $\sigma_{C-C} \rightarrow \sigma^*_{C-O}$ transition with charge transfer was involved. This assignment is supported by two additional arguments. Firstly, if we arrange the molecular states of acetone and, say, ethane on a single energy scale (ethane being chosen as the simplest model of an alkyl substituent containing the C–C bond), we find that the transition $\sigma_{C-C} \rightarrow \sigma^*_{C-O}$ falls exactly in the region of 55 000–60 000 cm^{-1} (see Fig. 11). Secondly, the intensity of the $n \rightarrow \sigma^*$ transition decreases[71] in the aliphatic ketone series as the intensity of the transition under discussion increases. Similar effects are found in cyclic ketones[73,74].

The carbonyl group in amides, acids, and esters is no longer an isolated chromophore. The absorption spectra of these compounds cannot be treated as an additive combination of the spectra of the elementary chromophores. The spectrum of formamide, in particular, consists of a broad band with a maximum at 1717 Å and a weak band with a maximum at 1345 Å.[75] The broad band has a fine structure some of whose components can be combined into a Rydberg series converging at 10.2 eV. The spectrum of dimethylformamide is similar to that of formamide but displaced towards longer wavelengths[75]. Nagakura assigned

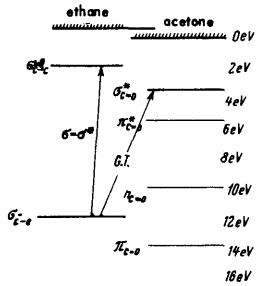


Fig. 11. Diagram of possible charge transfer in carbonyl compounds.

these bands[76] on the basis of the calculated electronic spectrum of formamide. Using the same calculation, the band at 1717 Å is shown to be associated with charge transfer and the band at 1345 Å with a $\pi \rightarrow \pi^*$ transition. Another paper by Nagakura and coworkers[77] gives the absorption spectra of formic and acetic acids and of ethyl acetate as well as the calculated electronic spectrum of formic acid. According to their calculation, the formic acid band with a maximum at 1590 Å is of $\pi \rightarrow \pi^*$ type to the extent of 46.2% and has 44.7% of charge-transfer character.

The  Chromophore

Aromatic compounds have attracted, not surprisingly, most of the attention of theoretical chemists. Benzene itself has undoubtedly been the object of practically every variant of the quantum-chemical methods. The basic difference between benzene and the chromophores discussed above is that the $2p\pi$ electrons in benzene cannot be localised at any individual carbon atom. All six $2p\pi$ electrons belong to the molecule as a whole. According to Pauli's principle, they should be distributed among three orbitals. Since these electrons are the least firmly bound in the molecule, their transitions should give rise to the long-wavelength part of the benzene spectrum. The simplest variant of the quantum-chemical calculation of the states of a π-electron system (the Hückel method) leads to a ground state in which the six π-electrons are distributed over two levels, the upper level being degenerate. The lower of the two nearest excited states is also doubly degenerate. Fig. 12 shows the energy diagram of the states and the shape of the corresponding molecular orbitals. The long-wavelength spectrum of benzene, reproduced in Fig. 13, is in fact determined by transitions to the

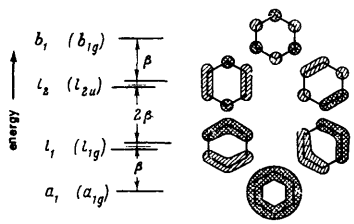


Fig. 12. Energy level diagram and orbital shapes in the benzene molecule[1].

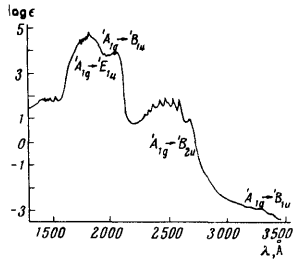


Fig. 13. Absorption spectrum of benzene[1].

two nearest excited states. The transition giving the longest wavelength is evidently forbidden on the grounds of change in multiplicity. The 2500 Å band is associated with the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition, forbidden by symmetry. The allowed $^1A_{1g} \rightarrow {}^1E_{1u}$ transition gives a band at 1800 Å, which is diffuse owing to predissociation. At still shorter wavelengths we find a fine structure caused by Rydberg absorption, and further still we find another Rydberg series[78]. Both these series converge to an ionisation potential compatible with the values obtained by other methods[26]. Platt and Klevens[79] studied the effect of alkyl substitution on the spectrum of benzene, and found that the 1800 Å band is gradually shifted towards longer wavelengths by alkylation in the sequence toluene, *o*-, *m*-, and *p*-xylene. The intensity of the observed band increases in the same order. The influence of lower symmetry on the spectrum of an aromatic system was investigated by El-Sayed[80]. As expected, the spectra of pyridine, pyrimidine, and pyrazine turned out to be more complex, but each of the changes, relative to the benzene spectrum, follows naturally from the lower symmetry which removes the degeneracy from an initially degenerate state. A review article by Stevenson[81] is devoted to the effect of chemical substitution on the electronic spectra of aromatic compounds, but, of course, it deals mainly with the near ultraviolet.

We have thus surveyed the spectra of practically all the most important organic chromophores. We must stress the fact that care was taken to avoid discussing substances in which several chromophores interact so strongly that they behave as a combined chromophore in which the characteristics of the components are lost. With this important exception, we may conclude that the chromophore concept remains a fruitful one in the far and vacuum ultraviolet. In other words, we can assign to each isolated functional group a fully characterised band or set of bands in the absorption spectrum which is an analytical criterion of this chromophore. Furthermore, we know in practically every case the qualitative and quantitative effect of the immediate environment, provided that it does not destroy the "isolation" of the chromophore being considered. The impact of intramolecular interactions on short-wavelength electronic spectra is undoubtedly of much greater interest, but unfortunately it is still too early to consider this topic: the fund of published data is too small. It should be remembered, however, that the far ultraviolet region is being intensively investigated at present, and the results should be available before long.

Our next question is: are the far and vacuum ultraviolet regions already of use to the chemist at the time of writing? In this connection we shall consider several examples of the practical application of short-wavelength electronic absorption spectra.

7. APPLICATION OF ABSORPTION SPECTRA IN THE FAR AND VACUUM ULTRAVIOLET TO THE ANALYSIS OF THE COMPOSITION AND STRUCTURE OF MATERIALS

The far and vacuum ultraviolet regions are the only source of information on electronic absorption spectra which can be applied to determining the composition of mixtures and the structure of compounds containing only saturated bonds (and which therefore do not absorb in the near ultraviolet and visible regions). Fig. 14 shows the spectrum of cholestanol[82]. The structural elements of this compound are cyclohexane and the hydroxy-group. Neither cyclohexane nor cyclohexanol have an absorption comparable to that of cholestanol. It follows that the excess absorption of cholestanol (as compared with cyclohexanol) can be ascribed to the quaternary carbon atom.

The isolated ethylene group gives an even more characteristic absorption. Cyclohexene and the sterols containing a cyclohexene ring (such as cholesterol and stigmasterol) give a band with a maximum at 180 nm (Fig. 15)[82]. Increasing the degree of substitution at the ethylene bond produces a monotonic shift of the band towards longer wavelengths, up to 200 nm.

The problem of the electronic structure of five-membered unsaturated heterocycles can be solved quite easily with the help of absorption spectra in the far ultraviolet.

Two structural variants of these compounds are possible. In the first the diene system does not interact with the heteroatom; in the second conjugation occurs between the n-electrons of the heteroatom and the π-electrons of the double bond. In the first case the absorption spectrum should be simply the sum of the spectra of the diene system and of the n-electrons. For example, the spectrum of thiophen should be indistinguishable from a superposition of the spectra of cyclohexadiene and tetrahydrothiophen. If the second variant is the correct one, the spectrum will have nothing in common with the superposition. Experiment settles the question unambiguously in favour of the second alternative. Thus, spectra in the far ultraviolet have confirmed the aromaticity of thiophen and selenophen[83].

Spectra in the vacuum ultraviolet have helped to characterise the main intermolecular interactions in solid ammonia, water, and methane. By comparing the spectra of the gaseous and of the solid compounds, it was found that hydrogen bonds play a very important role in the first two compounds, but are absent in the third[84].

Another very important aspect is that spectra in the far and vacuum ultraviolet provide information about a great

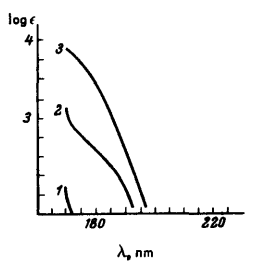


Fig. 14. Absorption spectra of cyclohexane (curve 1), cyclohexanol (curve 2), and cholestanol (curve 3)[82].

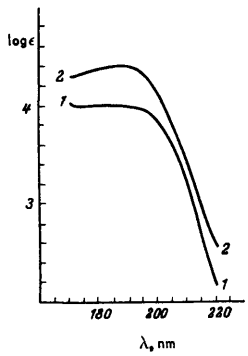


Fig. 15. Absorption spectra of cholesterol (1) and stigmasterol (2)[82].

number of molecular transitions. This adds substantially to the reliability of quantum-chemical calculations of the electronic structures and of the spectra themselves. The more we can check the predicted transitions the more realistic is the result of the calculation. Between three and five bands in the region 1500–2200 Å have been found in styrene, benzaldehyde, acetophenone, and benzonitrile. Satisfactory agreement with the observed spectra was obtained in a calculation which allowed for interaction between the ground state, a partially excited configuration, and a configuration including intramolecular charge transfer. The contribution of the charge-transfer configuration was 58% for styrene, and 68% for benzaldehyde (for the bands in the region of 2300 Å). The same investigation provided information about the electron affinity of the C=C and C=O groups.

In conclusion, we should mention another important field of application of the vacuum ultraviolet region: the determination of adiabatic ionisation potentials. In addition to the absorption spectra, which enable the Rydberg series to be observed and analysed, photoionisation spectra are also valuable in this context[26,27,86].

It should be understood that the applications listed here are only a very small fraction of the field and are given simply as illustration. The reader is referred to the bibliographic handbook published by Comstock in 1960 for a fuller review of the literature on this subject[87].

The analytical application of vacuum ultraviolet spectra in chemistry has been discussed in review articles by Kaye[88], and by Jones and Taylor[39].

References to the techniques and experimental methods can be found in the reviews by Price[89], Tousey[90], Lüscher[91], Inn[92], and Romand and Vodar[93].

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CHEMICAL COMPOSITION AND PROPERTIES OF IONIC CRYSTALS

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I. INTRODUCTION

An understanding of the effect of composition on the properties of chemical compounds of different types is essential in the development of new materials having prescribed properties. The problem is usually tackled with compounds of simple, known composition and structure, and the results are then applied to the more complex materials used in industry.

The classical theory of ionic lattices provides a satisfactory explanation of many of the physical properties of ionic crystals, such as the compressibility, polarisability, dielectric constant, wave propagation, spectra of characteristic ionic vibrations, etc., and gives practical formulae which can be used to evaluate these parameters. However, there is as yet no unified theory dealing from a single standpoint with the effect of composition on the thermal, mechanical, optical, and dielectric properties of solids.

Satisfactory theoretical explanations are available for a number of crystal properties not involving disturbance of the continuity of the lattice, but we lack a comprehensive theory of the mechanical disintegration, melting, or electrical breakdown of crystals, allowing the strength of the material to be calculated exactly and without assumptions, and giving values consistent with experiment.

The earliest theories were developed to explain individual properties of the solid state, usually without reference to each other: for example, the theory of specific heat or the theory of electrical breakdown, and also the theory of the elastic properties of crystals, without reference to the chemical composition of the material. Phenomena such as electronic and ionic electrical conduction, losses, breakdown, diffusion, etc. were not among the topics proper to solid state theory.

An essential stage in the development of a unified theory of the solid state is to compare the properties of crystals, to correlate them, and to establish a relationship between properties and composition.

The correlations between various properties of ionic crystals have been discussed extensively.

Kurnakov[1] suggested that the dynamics of changes in properties of the material should be observed on at least two parameters, because one property may be insensitive to the interaction in question under the particular conditions of the experiment.

Simple correlations were found between the composition and structure on the one hand, and the physical properties on the other hand, of organic compounds and polymers.

According to Butlerov's theory of the structure of organic compounds, the physical properties of materials depend on their composition and structure. For example, in one homologous series of saturated hydrocarbons increase of molecular weight raises the boiling point; the melting point also increases with the number of atoms in the molecule, and so does the density of the hydrocarbons at the boiling point[2-4].

Special structural features of monomers leading to the preparation of polymers with prescribed properties have been pointed out. For example, the addition of fluorine is known to enhance the thermal and chemical stability of polymeric molecules, although the resistance to radiation is sometimes lowered. A high proportion of cyclic groupings consisting of benzene rings in the polymer molecule raises the thermal and the radiation-chemical stability of the polymer. Hence, methods of preparation of polymer molecules with the highest possible content of fluorine atoms or of groupings containing benzene rings are now being intensively studied in polymer chemistry.

A study of the properties of ionic crystals and of their dependence on composition and structure is of practical importance for the description of inorganic materials in general and ceramics and glasses in particular. Materials of different physical structure can be obtained by controlling the composition and the treatment of a ceramic body. Ceramic materials have different mechanical, thermal, and electrical properties according to their composition and structure. The rules which control the relationship between the composition, structure, and properties of ceramics have not been adequately investigated.

Ceramic materials are a multiphase system, including a crystalline phase, an amorphous phase, and a gas phase (the pores). The composition, structure, and relative amounts of the phases determine the properties of ceramic materials in a complicated way.

The crystalline phase largely determines the physical properties of ceramics. Hence, studies of the properties of ionic crystals have great practical importance. The crystalline phase consists of chemical compounds and of solid solutions of the components found in many ceramic materials.

The most advanced dielectric properties are found in ceramics based on gemstone spinels ($MgO.Al_2O_3$), forsterite ($2MgO.SiO_2$), periclase (MgO), perovskite ($CaO.TiO_2$), clinoenstatite ($MgO.SiO_2$), etc.

Ionic crystals have found the most varied practical applications, as in the production of optical systems, in crystal counters, amplifiers, etc. A study of the properties of ionic crystals should advance our understanding of the fundamental properties of corrosion resistant, structural, and other ceramic materials, and of the relationship between the composition and properties of these materials.

It should also provide a scientific basis for the rational specification of their composition and method of treatment.

A solid is a quantum-mechanical system of strongly interacting particles. The individual properties of the particles in a solid are largely lost and replaced by new, collective properties which characterise the solid as a whole. The basic properties of the solid are determined by its chemical composition, physical structure, and by external conditions. The energy of interaction between the component particles of the solid, which controls its physical properties, is determined by the position of the constituent elements in the Periodic Table.

It is interesting to examine the way in which the physical properties of the simplest ionic crystals depend on the position of the components in the Periodic Table (i.e. on their atomic weight and atomic number). The bonding between particles in crystals is most conveniently expressed by the energy needed to remove each ion to an infinitely large distance from all the other ions. This quantity is termed the crystal lattice energy.

The early work was done on compounds which had been chosen without regard for similarities or differences between the properties of anions and cations, or for periodicity in their parameters. This has caused difficulties in comparing the results obtained by different workers, particularly since even individual workers have reported measurements made under different conditions.

Comparison of the results of different workers (particularly on the kinetics of various processes in ionic crystals) is further complicated by the choice of a single measurement temperature for compounds of different composition having different Debye temperatures. In such a case the crystal lattices are in different relative states of breaking up and of approaching fusion. In all probability, the properties of ionic compounds of different composition should be compared at their respective Debye temperatures or at a common relative temperature T_m/T_f, where T_m and T_f are the measurement temperature and the melting point of the crystal respectively.

The observed trends have led to attempts to generalise and to relate the properties of ionic compounds to their composition in terms of the lattice energy, free volume, ionic radii, atomic numbers of the component atoms, etc.

The present article aims to establish a correlation between various properties of ionic compounds taking the lattice energy as the characteristic parameter controlling the properties of ionic crystals. This parameter is thermodynamic and, therefore, macroscopic. In solid state theory the parameter is expressed in terms of ionic radii and ionic charges, and is therefore associated with the microscopic structure and composition of the compound.

In practice, the structures and composition of single crystals are always different from the ideal. It has been assumed[5] that the defects of a real crystal and their concentration are directly related to the lattice energy.

Ionic structures are close packed, so that ionic motion in the crystal is possible only by jumps into neighbouring vacant lattice sites. Motion of an ion by jumps in a given direction is accompanied by the transfer of vacancies of that ion in the opposite direction. The activation energy attending the motion of ion vacancies is a very important quantity which determines the displacement of ions and their vacancies from one equilibrium position to the next. This quantity increases, as a rule, with the ionic radius, but the potassium ion in sylvite is exceptional in having a very small activation energy[5]. As the lattice energy decreases, the activation energy needed to transfer an ion or vacancy from one position to the next also decreases. Hence we may conclude that a correspondence exists between the macroscopic description of these processes in terms of the lattice energy and the microscopic description in terms of the activation energy for the motion of ions and vacancies in the solid.

The properties of bodies obey an internal relationship which can be expressed by the equation of state for a real, inhomogeneous solid. To set up the equation of state of a solid body we need information on all the internal parameters of the system.

The observed correlation between the properties of ionic crystals and the lattice energy[5] can be described thermodynamically in terms of the expression for the free energy of an inhomogeneous body. Ignoring the vibrations of the ionic nuclei, the free energy of an ideal crystal consists of the energy density of the statistical lattice plus the zero-point vibration energy[1]. The equation of state of an ideal crystal, describing the relationship between pressure, volume, temperature, thermal and mechanical properties, can be derived from the expression for the free energy. The free energy at low temperatures is determined by the internal energy, i.e. by the potential energy of the interacting ions at 0°K, which we call the crystal lattice energy.

Like many other properties of a crystal, the entropy also is related to the lattice energy. Hence the free energy in the linear approximation is expressed in terms of the lattice energy[7].

In the theory of crystal lattices the free energy is used to define the linear temperature expansion coefficient and the isothermal compressibility, which are related to other mechanical, thermal, optical, and electrical characteristics of the crystal. Hence, the relationship between various physical characteristics of a solid and changes in its free energy can be established thermodynamically[6].

It follows from what has been said that the relationship between the normal mechanical, thermal, optical, and electrical properties and the free energy can be replaced by a relationship between those properties and the lattice energy, the latter being simpler to determine. The lattice energy is proportional to the product of the valencies and inversely proportional to the sum of the ionic radii and depends only on the chemical composition and structure. Expressions for the properties of bodies in terms of the lattice energy reflect their dependence on chemical composition.

The free energy of a real solid differs significantly from the ideal value on account of the energy stored in defects. The defect structure is one of the properties of real crystals. Like other properties, the defect structure of crystals, characterised by the concentration of defects, is related to the lattice energy and under different measurement conditions this relationship can upset in various ways the dependence on lattice energy of a basic characteristic[8].

When defects form, energy is absorbed by the crystal and the internal energy increases. At the same time, point defects raise the configurational entropy of the system. Hence, the free energy of the system can decrease at high temperatures as a result of the increase in entropy[9] The excess of internal energy arising from the formation

of point defects in the ionic lattice increases with the concentration of defect pairs. The concentration of defects increases with deformation, irradiation, and increase of temperature. It decreases with radiational and thermal annealing.

The establishment of a correlation between various characteristics of ionic crystals in terms of the lattice energy alone is of practical importance, since it would enable a comparison of the changes in properties of ionic compounds resulting from changes in chemical composition. A satisfactory classification of the different ionic compounds according to their properties can be based on a single parameter: the lattice energy. When the relationship between the properties is known, the lattice energy can be used to determine many other properties of ionic crystals of practical importance.

II. CRYSTAL LATTICE ENERGY AND SURFACE ENERGY OF IONIC CRYSTALS

The stability and the strength of a crystal depend on the magnitude of the forces acting between the particles, and on the crystal lattice energy which is determined by these forces. For ionic crystal lattices of the same structural type, the energy of the bond between the particles is determined by the chemical composition. The energy of the crystal lattice is a valuable index of the energy level of the system.

In the classical Born–Madelung theory of ionic crystals [10,11] the interaction energy is determined by the electrostatic interaction between all the ion pairs. The interaction energy is calculated taking account of the electrostatic Coulombic attraction energy e^2/r (for charges of different sign) and of repulsive forces (for charges of the same sign). The energy of the repulsive forces due to the electron shells of the ions, B/r^n, is then computed.

In the calculation of the forces of attraction and repulsion acting between a cation and an anion the energy of the ionic lattice is given by the formula

$$U = -\frac{N}{2}\left[\frac{A\,\eta_1\,\eta_2\,e^2}{r_0} - \frac{B}{r_0^n}\right] \qquad (1)$$

where A is the Madelung constant, which depends on the crystal structure, η_1 and η_2 are the valencies of the ions of which the lattice is composed, r_0 is the shortest distance between the centres of oppositely charged lattice ions, n is the exponent in the expression for the potential of the repulsive forces, B depends on the crystal structure and on the structure of the ion, and N is the number of ions in the crystal. The magnitude of the repulsive force is determined by the distribution and by the number of electrons in the outer shells. The exponent n is greater for Na^+ ions, which have 8 electrons in the outermost shell, than for Li^+ ions, which have only 2 electrons.

The complete expression for the crystal lattice energy, including quantum-mechanical corrections, is an additive function of the energy of the electrostatic attraction forces, the energy of the repulsive forces, the energy of the van der Waals cohesive forces between ions, and the zero temperature vibrational energy. The vibrational energy of a lattice consisting of N atoms at absolute zero is $9h\nu N/4$, where ν is the residual radiation frequency and h is Planck's constant.

Thus, the full expression for the lattice energy at 0°K of an alkali metal halide crystal per mole can be written [2]

$$U = N\left[\frac{\eta^2 e^2 A}{r_0} + \frac{C}{r_0^6} - B(r_0) - {}^9/_4 h\nu\right] \qquad (2)$$

where U is the lattice energy, η^2e^2A/r_0 the part of the energy arising from electrostatic attraction, η the lowest valency found in the lattice, C/r_0^6 the van der Waals energy, and $B(r_0)$ the potential energy due to the repulsive forces in the lattice.

Calculations of the lattice energy by formulae (1) and (2) involve serious difficulties in the determination of the value of r_0 by X-ray diffraction and in the computation of the quantities A and n.

Kapustinskii [12], using Born and Mayer's quantum-mechanical expression for the lattice energy, derived an equation for the energy of a crystal lattice not involving A or n:

$$U = 287.2\,\frac{\Sigma m \eta_C \eta_A}{R_A + R_C}\left(1 - \frac{0.345}{R_A + R_C}\right), \qquad (3)$$

where Σm is the number of ions in the molecule and η_A, η_C, R_A, and R_C are the valencies and the radii of the anion and the cation respectively.

The majority of inorganic compounds are not usually ionic. In ionic crystals we observe a continuous transition from ionic to covalent bonds, but there is no satisfactory criterion for determining the degree of polarity.

Sarkisov [13] proposed that the lattice energy of ionic compounds should be calculated on the basis of the electron gas concept, in which the ionic bond is, effectively, replaced by a covalent bond. Any crystalline inorganic compound is envisaged as an assembly of cores of interacting atoms: the chemical bond between the atoms is created by an electron cloud formed by the delocalisation of the valency electrons of the metal atoms and of an equivalent number of peripheral electrons from the non-metal atoms. The chemical bond in a lattice of the NaCl type is described as a strongly polar covalent bond. The electron cloud of the bond between the sodium and chlorine atomic cores consists of two electrons, made up of one valency electron from the sodium and one peripheral electron from the chlorine. In homopolar crystals the maximum density of the electron cloud of the bond is located exactly half-way between the neighbouring nuclei, and in typically ionic crystals it suffers a maximum displacement towards the non-metal. When this shift occurs, the electron cloud cannot be considered to belong exclusively to the non-metal, but the motion of the electrons must be treated in the field of the two positively charged cores of the interacting atoms.

Thermochemically, the lattice energy is defined by the Born–Haber cycle.

The lattice energy of chemical compounds varies in accordance with the periodicity of the properties of their constituent elements in the Periodic Table. Fig. 1 shows the change in lattice energy with composition for the alkali metal halides. An increase in the size of the ions (and therefore in the size of the unit cell) is accompanied by a decrease in lattice energy. Replacing the anion whilst keeping the cation constant, or replacing the cation whilst keeping the anion constant, produces a monotonic change in lattice energy. This substitution causes the lattice energy to decrease as the sum of the atomic numbers of anion and cation ($Z = Z_C + Z_A$) increases, and to approach a constant value for large Z. However, if we go to the halides of

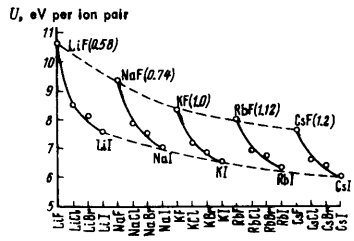


Fig. 1. Variation of lattice energy with composition for the alkali metal halides. (The numbers in brackets denote the cation to anion radius ratio.)

another metal or to the compounds of metals with other halogens we land on a different curve.

There are several rules which describe the change in lattice energy of a chemical compound with composition. Increase of ionic charge raises the lattice energy. The lattice energy of alkali halide crystals, consisting of singly charged ions, is 100–200 kcal mole^{-1}. The lattice energy of metal oxides such as MnO, FeO, NiO, and others, composed of doubly charged ions, is ~ 900 kcal mole^{-1}.

Compounds of the cations of secondary subgroups, with 18 electrons in the outer shell, have a greater lattice energy than compounds with ions of the same period but having the inert gas structure, thus [5]:

$$U_{CuCl} > U_{KCl};\ U_{ZnBr_2} > U_{CaCl_2}.$$

This rule probably follows from the smaller size of the ions in the secondary subgroups, and particularly from the influence of the polarisation energy, which is evident also from the following rule. The lattice energy of the halides of secondary subgroup elements is much less sensitive to anion radius than that of the main subgroup elements. If the radius of the anion increases, the lattice energy should decrease. However, the polarisation energy also increases, and in the secondary subgroup elements this has a much more profound effect than in the main subgroup elements.

Quantum-mechanical corrections to Born's theory have enabled us to calculate the vibrational energy of the crystals at 0°K and the contribution to the attractive energy from van der Waals dipole–dipole or dipole–quadrupole interaction, amounting to several per cent of the total lattice energy. In silver halides this additional term in the interaction energy is very much greater because of their large polarisability, and reaches 14% in AgBr. The correction for the van der Waals interaction forces in these compounds is greater for the heavier elements, which experience a greater polarisation. The correction for zero-point energy is greater for compounds composed of light elements, which have a higher Debye characteristic frequency. Therefore, a change in composition in the alkali and alkaline-earth metal halide series is accompanied by a change in the role of a given type of chemical bond in the compound, which in turn induces a change in the properties of the compound.

The lattice energy is linearly related to the heat of formation [10]. Oxides having a low heat of formation (and therefore a low lattice energy) are likely to be semiconductors. These include Ag_2O, CuO, NiO, CoO, FeO, CdO, HgO. Oxides with a high lattice energy and heat of formation (CaO, MgO, ZnO, BeO, BaO, SrO) are dielectrics of high electrical and mechanical strength.

The rates of processes depending on the thermal mobility of atoms in diatomic and polyatomic systems are related to interatomic interactions. The rates of processes depending on the thermal motion of atoms are functions of lattice energy.

The most stable structures are obtained by forming compounds of tetravalent elements. The oxides of Group II elements of the Periodic Table, BeO, MgO, CaO, SrO, BaO, have high lattice energies, heats of formation, melting points, and also good electrical and mechanical properties.

The lattice energy determines: (a) the tendency to form stable heteropolar lattices; (b) the mechanical strength of the compounds; (c) the stability of the compounds towards melting, but not necessarily towards dissociation, and (d) the solubility in aqueous solutions. However, the lattice energy cannot completely define the stability of the system. Polarisation and depolarisation phenomena must also be taken into account: these can have a considerable influence on the ionic radius and therefore on the course of various processes. Lattice energy depends on the crystal structure [14].

The lattice energy is lowest for lattices of the caesium chloride type, and highest for wurtzite. This increase in lattice energy corresponds to a decrease in the ionic radius from 1–0.7 (for a caesium chloride type lattice) to a value below 0.4 (wurtzite). The modern theory of the crystal lattice and well-known experimental results provide the data needed to compare the properties of ionic lattices with their energetic and structural characteristics [15].

The surface particles of a solid experience considerable forces of attraction from particles in the interior. This attraction is not compensated by attractive forces from particles in the surrounding medium. Hence, the particles on the surface have a greater potential energy than the particles in the interior of the body. The excess energy of the surface particles can be determined by transferring particles from the interior to the surface. When a crystal is broken into pieces the work required to transfer particles to the surface has to be expended [15].

The specific surface free energy is measured by the work done in creating 1 cm^2 of surface layer by an isothermal process and is different for different crystal faces. For crystals of the rock salt type, the specific surface energy of the cubic face, $\sigma_{(100)}$, is lower than that of the rhombic dodecahedral face, $\sigma_{(110)}$, or of the octahedral face, $\sigma_{(111)}$. If molecules of active substances are adsorbed on the surface of a solid the specific surface energy of the face decreases. The surface energy of crystals decreases after irradiation.

The surface energy has a considerable effect on the course of many processes taking place at the interface between two solids, especially on phenomena involving the formation or disappearance of a surface, diffusion, adsorption, etc. By its physicochemical nature, the surface energy is a manifestation of interaction forces and of chemical bonding between particles, and can be calculated by applying the formulae for the lattice energy.

The surface energy is small compared with the lattice energy. To divide one mole of rock salt into small cubes

of linear dimensions of the order of one micron, thus imparting to it a surface area of 1.62×10^6 cm^2, requires the expenditure of only 0.0057 cal, whereas the lattice energy is [16] 183 kcal mole^{-1}.

The surface energy is relatively unaffected by changes in composition. Hence, pronounced changes in properties with chemical composition must be associated with lattice energy rather than with surface energy, the latter being relatively insensitive to the composition of the material [15].

III. CORRELATION BETWEEN PROPERTIES OF IONIC CRYSTALS AND LATTICE ENERGY

The properties of ionic structures are interrelated, but the rules which govern these relationships have as yet been theoretically established in only a few cases. Hence, until quite recently, the various properties were investigated in most cases separately. During the last decade complex studies of different properties and of their interplay have become more frequent [15,16].

On heating, applying mechanical or electrical stress, or on dissolution, the bonds between the particles in an ionic crystal are overcome, which leads to the collapse of the lattice. The energy needed to break down the lattice depends on the forces between the particles which form the lattice. An increase in lattice energy leads to enhanced mechanical, electrical, and thermal stability in ionic compounds. These results were obtained from measurements on single crystals and compacts pressed from powdered oxides, sulphides, and halides of metals of Groups I and II.

The lattice energy determines the physicochemical properties of a crystal involving separation of the ions, their motion in the lattice, and changes in interaction forces between the ions.

The plastic properties of solids are described by the dislocation theory. The mechanical properties of real crystals vary in a regular manner with lattice energy, which characterises the ideal lattice. This correlation exists because structural defects, their concentration and mobility, and dislocations are all determined by the same structure and are related to its energetics [17].

The polarisability and the chemical bonding between ions depend on the nature of the ions. In a series of metal halides of a single type the polarisability decreases on going from rubidium to lithium compounds and increases as the anionic radius increases from fluorine to iodine [18].

Changing the structural type of the rubidium fluoride lattice, which has the caesium chloride structure at normal temperature and pressure, does not disturb the overall regularity. Associated with changes in the polarisability and concentration of the ions, the dielectric constant and its electronic and ionic components are found to increase or decrease as the lattice energy increases.

The electrical conductivity of ionic compounds in the solid state is determined by the motion of cation vacancies both in the intrinsic and in the impurity region. The heat of activation for electrical conduction, measured from the temperature coefficient of conductivity, increases as the lattice energy increases, whilst the magnitude of the conductivity decreases. The temperature of onset of intrinsic conduction in ionic compounds is shifted upwards as the lattice energy increases.

Dielectric loss arising from conduction at low or at high frequencies behaves similarly. An explanation has been given [19] of observed discrepancies from the general pattern, due to impurities, including the formation of vacancy aggregates, the distribution of impurities throughout the crystal, etc.

The specific heat and the heats of fusion, sublimation, evaporation, and dissociation increase as the lattice energy of ionic compounds increases, whilst the linear thermal expansion coefficient decreases [5].

The electronic component of the dielectric constant of alkali metal halide crystals increases as the polarisability of the halogen is increased (keeping the metal constant) and the lattice energy is decreased.

The replacement of magnesium by calcium, strontium, etc. in titanates produces an increase of dielectric constant, accompanied by a decrease of the binding energy of the particles in the lattice [19].

In crystals, the physical phenomena determined by the elastic vibrations of ions are related to the lattice energy. The specific heat per g-atom of compounds of metals of Groups I and II decreases as the lattice energy increases. The melting points of alkali metal halide crystals increase with the lattice energy. The fundamental vibration frequency of the lattice ions of the compounds of metals from Groups I and II also increases with the lattice energy.

The surface energy has a substantial effect on many processes occurring at the contact between two solids. The surface energy can be considered, physicochemically, as the manifestation of the interaction forces between particles and of the chemical bond between them. Hence, the crystal lattice energy and the surface energy of a solid in a vacuum are interrelated. Any increase in specific surface energy is accompanied by an increase in lattice energy. A successful attempt has been made [20] to relate the surface resistance of solid dielectrics to the value of the surface energy.

High values of the lattice energy and surface energy in ionic compounds cause hydrophilicity and increase the surface conductivity. They also degrade, in general, the favourable electrical properties of ionic dielectrics. The highest surface resistivity is found in materials having a structure intermediate between those of materials with ionic and with atomic bonds (for example, in fused quartz).

When the binding energy of ions in the lattice increases, the electrical conductivity and dielectric losses of ionic crystals decrease.

Some crystal properties, e.g. thermal conductivity, specific heat, elastic moduli, etc., are determined not so much by the lattice energy as by its derivatives with respect to various parameters. Due to the simple relationship between the properties of ionic crystals and the lattice energy, the various properties are also simply interrelated. A knowledge of the lattice energy allows a complicated evaluation of the properties of ionic compounds of a given series. Compounds with a high lattice energy have more desirable properties in practice. For example, beryllium and magnesium compounds are more refractory and have a higher mechanical and dielectric strength than barium or zinc compounds [19,21-29].

However, not all the properties and characteristics of ionic crystals can be simply correlated with lattice energy. Processes in which ionic compounds are broken down to

atoms or radicals rather than ions do not show a simple correlation. For example, the stability of azides towards thermal decomposition increases from lithium to caesium azide, i.e. on going from compounds with higher towards compounds with lower lattice energy [30]. The heat of formation increases from lithium towards caesium [31]. In this case the failure of the rule according to which the stability of ionic compounds should increase with the lattice energy can be explained as follows. Azides decompose into atoms as a result of electron transfer from the anion to the cation. Hence the elementary act is ionisation of the anion, followed by the collapse of the lattice. The sign of the ionisation potential is opposite to that of the lattice energy, and its magnitude varies more markedly than the lattice energy from cation to cation. When the azides are decomposed into ions (e.g. in aqueous solutions) their stability is found to increase in the same sense as the lattice energy [32].

Departures from the simple correlation between lattice energy and various physicochemical characteristics are observed also when the compound includes chemical bonds of different types and strengths. Among such compounds we find, for example, the crystal hydrates, in which coordinate bonds are present as well as ionic bonds. The stability of these compounds towards mechanical, thermal, chemical, and electrical breakdown increases with the number of water molecules present in the lattice, because this increases the strength of the bond between the particles of the lattice.

The weak van der Waals bond between the layers of layered structures explains the low strength of these materials towards cleavage along the layers. When such a body is fractured across the layers, against the large coulombic interaction forces, the strength is found to be high [17,18,20,33].

The exceptions which we have considered allow us to formulate more precisely the rule for the stability in a series of chemical compounds of a single type: when the compounds are broken down into their structural units (for example, ions in the case of an ionic lattice), the stability is found to vary in the same order as the strength of the bond between the structural units.

Homopolar lattices can form a strong framework made up of covalent bonds (diamond lattice). Unlike compounds having an ionic lattice, homopolar compounds retain their dielectric properties in the melt. The main physicochemical and electrical properties of solids with a homopolar lattice depend on the parameters of their constituent atoms (radius, deformability of electronic shells, etc.). Thus, for example, in Group IV carbon (diamond) is a good insulator, silicon (which crystallises in the diamond lattice) is a semiconductor, and tin has the electrical properties of a metal. The quantity equivalent to the lattice energy of ionic crystals is, in homopolar materials, the energy of atomisation, i.e. the energy needed to dissociate the atoms forming the homopolar lattice (or the energy needed to convert these materials into a monatomic vapour).

The physicochemical properties of homopolar structures are determined by the heat of atomisation and depend on the parameters of the constituent atoms [34-39].

In a molecular lattice, as well as in crystals with mixed ionic and covalent bonds in comparable proportion, no simple correlation is found between the overall binding energy and the physicochemical characteristics of the material. Most practically useful materials are compounds of this type.

The lack of simple, unique correlations between the physicochemical properties and the energy of the bond between the particles of compounds having chemical bonds of different types probably follows from the fact that the role of the various bonds is different under different external interactions. Some processes reflect one type of chemical bond, other processes reflect the other.

The physicochemical properties of liquid and of gaseous organic compounds have been compared with their dielectric strength. In the alkane series the dielectric strength increases with the strength of the bonds between molecules, and is practically independent of the strength of the intramolecular bonds. From these results, the electrical breakdown of organic dielectrics has been visualised as a process which begins with the breaking of intermolecular bonds. As the energy becomes concentrated in a discharge channel, breakdown may involve the breaking of intramolecular bonds [39].

The fact that the properties of real crystals depend on defects as well as on the lattice energy stems from the influence of the energetics of the crystal lattice on the behaviour of defects (in particular, of dislocations). Dislocation theory shows that the size and mobility of a dislocation are determined by the forces between the constituent particles of the crystal. The density of dislocations in crystals grown from the melt decreases as the crystal lattice energy increases.

The influence of defects and of the lattice energy on the electrical properties of ionic crystals has been established in the case of electrical conductivity. In ionic crystals, current is carried almost exclusively by cation vacancies [40]. Under these conditions, the conductivity is determined by the number of cation jumps per unit time. This number is proportional to the probability of a cation adjacent to the vacancy having sufficient energy for the jump. The concentration of vacancies in the crystal is proportional to

$$\exp\left(-\frac{W}{2kT}\right),$$

where W is the work of formation of a vacancy pair.

This quantity is related to the energy of the crystal lattice, and this accounts for the dependence of the electrical conductivity of alkali metal halide crystals on lattice energy.

As the lattice energy increases, both the electrical conductivity and the conductance losses in alkali metal halide crystals decrease.

The relation which exists between the defect structure and the energy of a crystal lattice leads us to expect that the laws derived for single crystals will be found to be equally applicable to the polycrystalline substances used in technology. In polycrystalline samples of oxides and halides of Group II elements, prepared by pressing followed by heat treatment, the electrical conductivity and the dielectric losses decrease as the lattice energy increases, and at the same time the activation energy increases.

Ceramic materials and minerals in which the binding energy between ions is large have a high thermal and chemical stability and high mechanical and dielectric strength.

The stability towards neutron bombardment of the properties of beryl, quartz, phenacite, chrysoberyl, barium titanate, and other minerals decreases in the following

order: beryllium–oxygen, silicon–oxygen, aluminium–oxygen, titanium–oxygen, zirconium–oxygen, and barium–oxygen. The decrease in radiation stability of the oxides is accompanied by a corresponding increase in cation radius: Be (0.34 Å), Si (0.39 Å), Al (0.57 Å), Ti (0.64 Å), Zr (0.87 Å), Ba (1.43 Å).

Replacement of the cation in this sequence also lowers the ionic bond character and the lattice energy per ion [41-43].

IV. STORED ENERGY IN IONIC CRYSTALS

The energy absorbed by crystals during mechanical or heat treatment, or irradiation, causes heating or the formation of various types of damage to the lattice: this increases the internal energy of the crystal and the elastic deformation energy. In particular, after irradiation a crystal has an excess of free energy (over the equilibrium value) which is termed latent or stored energy. The amount of stored energy is related to the radiation-induced defects: it can be used as a measure of the number of these defects, and it controls the change in physical and chemical properties of the material.

Compounds having a relatively large effective atomic number form crystals of relatively low lattice energy. When subjected to a given dose of radiation, these crystals absorb more energy than crystals with a high lattice energy.

Because defects are annealed more rapidly in crystals of low lattice energy, the stored charge at room temperature is smaller than in crystals with a higher lattice energy.

If the energy of formation of a defect is known, the number of defects can be determined by measuring the total stored energy. If the number of defects is known, the energy of formation of a single defect can be calculated. Provided the irradiation is carried out at low temperature, when the annealing of defects is suppressed, the stored energy is a measure of the energy of formation of the given number of defects. Radiation damage to solids is in some respects analogous to the influence of plastic deformation, and is attended by similar changes in properties. In contrast to cold working, radiation damage has the following characteristics: (1) it causes a different type of microscopic damage to the lattice; (2) radiation damage is more extensive than the damage caused by plastic deformation; and (3) radiation damage appears in a microscopic volume, and is not crystallographically oriented [41].

After a high integral dose of neutron irradiation, spallation of the crystals was observed. The minimum dose of radiation needed for significant breakdown of the crystals into blocks increases with the stability of the crystals (i.e. with the lattice energy). For quartz and for lithium fluoride the dose was, respectively, 1×10^{19} and 8×10^{17} neutrons cm^{-2}. [42]

The energy stored in rock salt after 6.64% relative plastic deformation at room temperature and a maximum stress of 1.02 kg mm^{-2} was 0.4 J g^{-1}. Less than 10% of this energy is stored in point defects [43].

The stored energy increases the free energy and weakens the cohesion of the lattice. Hence, the Debye temperatures (calculated from X-ray diffraction data) of undeformed and deformed crystals of rock salt are 260–290° and 150–170° respectively [44,45].

When the concentration of F-centres was increased from 2.5×10^{17} to 6.5×10^{17} cm^{-3} by irradiation with X-rays the stored energy was found to increase linearly [46], with a tendency towards saturation at higher doses.

On annealing NaCl crystals containing stable vacancy complexes, maxima were observed on the curve of heat evolution versus temperature. These corresponded to the annihilation of mobile defects at the lower temperatures and to dissociation of the vacancy complexes at the higher temperatures [47,48]. The stored energy was measured in crystals which had been irradiated with 4.3 MeV protons in a flux of 1.5×10^{14} protons cm^{-2} s^{-1}, with X-rays, and with γ rays from ^{60}Co. Single crystals of CaF, SrF_2, BaF_2, LiF, NaCl, KCl, KBr, and KI, and of solid solutions in the KCl–KBr system, were investigated. The measurements were made by annealing and also, in the case of the alkali metal halides (with the exception of LiF), by dissolution in water as well as by annealing.

Fig. 2 shows the temperature variation of the rate of evolution of heat from NaCl crystals, heated after the stated dose of ^{60}Co γ radiation. As the dose was increased, the amount of energy stored in the crystal increased, and the first (low-temperature) peak grew. The stored energy was greater in the crystals with the higher lattice energy. The amount of energy stored increases with dose of radiation. In crystals with a large lattice energy the stored energy accumulates faster than in crystals with a smaller lattice energy.

Several times more energy is stored in alkali metal halide crystals than in copper crystals, probably because of energy scattering by the free electrons in copper. The difference may be associated with the nature of radiation damage in alkali metal halides under X-ray irradiation. The defects are formed in these crystals by ionisation processes, which consume 99% of the absorbed energy. In copper the radiation damage occurs mainly by elastic interactions between the particles and the atoms of the material.

The energy stored upon irradiation can be as much as 7% of the lattice energy in NaCl. The energy stored in NaCl after irradiation at room temperature can be 200 times higher than the energy stored under maximum plastic deformation. As the temperature is lowered the amount of stored energy increases. Irradiation is a much more powerful agency than plastic deformation [49-52].

In NaCl + Ca crystals irradiated with X-rays the stored energy increases with increase of the calcium content. The position of the peak rate of heat evolution of the temperature axis shifts towards lower temperatures when the concentration of impurity is increased. This result is in keeping with the hypothesis that the activation energy for

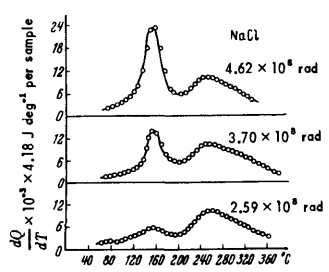


Fig. 2. Variation of the rate of evolution of heat with temperature on heating NaCl crystals irradiated with γ rays [46].

annealing radiation damage is smaller in the presence of impurities [52].

The stored energy after irradiation in solid solutions is less than in the original, pure crystals. Hence, crystals of solid solutions are more stable to radiation than pure crystals.

The amount of free energy which can be stored in the structure is determined by the experimental conditions and by the composition of the compound. As the bond energy increases, the energy storage capacity (i.e. the free energy) of the crystal increases. Substances having a high lattice energy and able to store the energy dissipated by mechanical or thermal treatment, or by irradiation, can be used as memory elements for external interactions giving rise to excess free energy.

The radiation-induced changes in the properties of materials with ionic bonds vary in the same sense as the stored energy. The amount of energy stored after relatively low doses of radiation or by quenching is of the same order of magnitude as in systems containing impurities or in solid solutions. Thus, solid-state reactions, whose characteristics show a correlation with the free energy in ionic compounds, are influenced by irradiation in the same way as by heat treatment.

The postulated strong influence of the after-effects of irradiation on the rate of processes determined by free-energy changes, and the expectation of a significant change in the properties of substances with bonds of the ionic type, were not confirmed by experimental measurements. The changes taking place in the material during irradiation are determined by the amount of energy absorbed: this increases as the lattice energy of the crystal is decreased. A compound with a low bond energy absorbs more energy in the radiation field and is weakened to a greater extent than a compound with a higher lattice energy. The energy absorbed exceeds the stored energy by two or more orders of magnitude. Hence, radiation technology should be based on the effects occurring during irradiation rather than after irradiation [41].

V. DISSOLUTION AND EVAPORATION OF ALKALI METAL HALIDES

When alkali metal halides come into contact with water or unsaturated aqueous solutions the following processes can occur: diffusional or diffusion-kinetic dissolution, hydrate formation, dissociation, and crystallisation from solution. The probability and rate of each of these processes depend on the bond energy of the chemical compound being dissolved, on the nature of the solvent, and on the dissolution conditions.

When a crystal dissolves and the system passes from an ordered to a disordered state the energy of the system increases. The ordered state of the particles in the crystal corresponds to a minimum in potential energy.

The heat of solution Q_{sol} is made up of the heat needed to break down the crystal structure, including the lattice energy U (taken with the negative sign) and the heat of interaction of the solute with the solvent ($H > 0$), which is evolved on dissolution. Thus, we have approximately

$$Q_{sol} = H - U. \qquad (4)$$

On dissolution in water with formation of hydrates the quantity Q_{sol} [*H*? (Ed. of Translation)] is termed the heat of hydration.

Fig. 3 shows the variation of the heat of hydration of the alkali metal halides, taken as the sum of the heats of hydration of the ions, with the lattice energy. The expected linear relationship (4) is satisfactorily supported by the experimental data (see Fig. 3).

The chemical stability of ionic compounds increases with increase of lattice energy [5]. The monotonic relationship between solubility and thermal effect is infringed if compound formation with water takes place [5]. If the salts dissolve without forming hydrates, and dissolution occurs with absorption of heat, i.e. $\Delta H > 0$, the solubility decreases with increase of lattice energy as shown in Fig. 4. For compounds which form crystal hydrates the thermal effect on dissolution increases with increase of lattice energy.

For aqueous salt solutions, if $\Delta H > 0$, we also have $T\Delta S > 0$, where ΔS is the increase in entropy of the system resulting from dissolution [53]. The thermal effect on dissolution of these systems, coupled with the condition $T\Delta S > \Delta H$, automatically controls the dissolution. The large increase in entropy of the system during dissolution of a crystal lowers the free energy of the system and therefore favours the dissolution process. The entropy increase ΔS attending dissolution in water of the alkali metal halides which do not form hydrates is smaller, the higher the lattice energy. This accounts for the decrease in solubility illustrated in Fig. 4.

Crystals of alkali metal halides can dissolve in water and in aqueous solutions in the diffusional regime when the rate of dissolution is determined exclusively by diffusion, and in the diffusion-kinetic regime, which depends on the structure of the crystal [54].

The difference in the dissolution mechanism of crystals along different crystallographic directions gives rise to

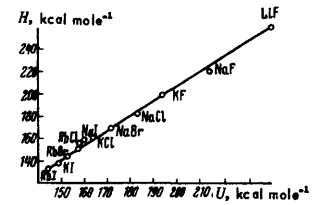


Fig. 3. Variation of the heat of hydration of alkali metal halides, taken as the sum of the heats of hydration of the ions, with lattice energy.

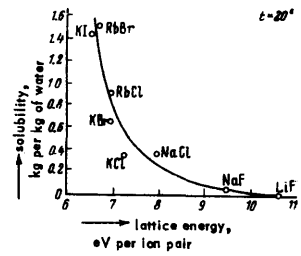


Fig. 4. Solubility of the alkali metal halides in water at 20° against lattice energy.

anisotropy in the rate of dissolution. The rate of dissolution of a crystal in the mild solvents recommended for etching is probably more under the control of the reaction by which particles are transferred from the crystal into the solution than under the control of diffusion into the bulk of the solution [31,55].

In the diffusion-kinetic regime the rate of dissolution of a crystal becomes anisotropic. At room temperature the highest rate of dissolution is observed on the (110) face, and the lowest on the (100) face. The ratio of the rates $v_{(110)}$ and $v_{(100)}$ increases [with lattice energy? (Ed. of Translation)] [31]. The rate of dissolution is highest when the reticular density of the ions on the crystal face is highest and the energy of the bonds between the ions is lowest. The rate of dissolution is lowest on the (110) face, which has the highest density of ions, but on the other hand the bonds between the ions on the (100) face are the strongest [sic]†. Thus, the rate of dissolution in this case correlates satisfactorily with the bond energy of the ions, but not with their density. In the (110) plane the rate of dissolution is greatest, the ionic density is less than on the (100) face, and the bonds between neighbouring ions are less strong than on the (100) face. Therefore, we again note a satisfactory correlation between the rate of dissolution and the energy of the bond between the particles [31].

The dissolution anisotropy of crystals increases with increase of surface energy and of lattice energy. The rates of contact melting of the various faces of crystals display a similar relationship to that of the rates of dissolution of the faces: the rate of contact melting of the crystals is a maximum on the (110) face and a minimum on the (100) face [7-9]. The ratio of the dissolution rates, $v_{(110)}/v_{(100)}$, for a given undersaturation increases with the crystal lattice energy. Therefore, the transition to the diffusion-kinetic dissolution mechanism takes place at lower concentrations in the aqueous solutions used as solvents [31] when the lattice energy of the crystals is greatest. When the crystals are dissolved in doubly distilled water the anisotropy $v_{(110)}/v_{(100)}$ of the rate of dissolution increases with the lattice energy and with stirring rate of the solution.

In radiation chemistry and technology it is important to know the dissolution mechanisms of materials during and after irradiation. The damage to the structure of an irradiated crystal leads to an increased density of dissolution centres and to a higher rate of dissolution under certain conditions. The (100) and (110) faces, which contain ions of both kinds, were chosen for comparison: the (111) plane contains only ions of a single kind.

The interionic distance on the (110) face is greater than on the (100) face by a factor of $\sqrt{2}$, and the bond energy is accordingly lower. The density of defects is greater on faces with a lower bond energy. Because of its lower bond energy and higher defect concentration, the (110) face dissolves faster than the (100) face [56].

Because of the bond energy differences in the various crystal planes, in practice a crystal always breaks along a (100) cleavage plane, whose bond energy is lower than that of alternative planes. This is because the bond energy between ions in neighbouring (100) planes is decreased by the relatively large interplanar spacing. Irradiation of a crystal with soft X-rays, which are absorbed in a thin layer, increases the linear rate of dissolution of the (100) face without affecting the rate of dissolution of the more defective (110) face. For any given rate of arrival of the solvent flow at the surface undergoing dissolution, and for each crystal composition, we can define a limiting undersaturation σ_0 of the solvent. The linear rate of dissolution of a (100) crystal face is affected by irradiation only if the relative undersaturation is less than σ_0.

The value of σ_0 increases with lattice energy. To remain in the region of low dissolution rate, in which the rate is a function of the previous dose of radiation, the degree of undersaturation of the solvent must be lowered in proportion to the energy of the chemical bond [55].

These results justify the general conclusion that the linear rate of dissolution should be structure-sensitive at low dissolution rates and low undersaturations of the solvent [31].

Fig. 5 shows curves for the relative linear rate of dissolution of an irradiated (100) face (v_0/v_n, where v_n is the rate before irradiation) for various values of the relative undersaturation σ and for crystals of different chemical composition after irradiation with a dose of 10^5 rad of 8 keV X-rays. Irradiation and dissolution were both carried out at room temperature.

The largest increase in rate of dissolution is found in crystals with high lattice energy. This result agrees with the hypothesis that radiation-induced defects, which increase the rate of dissolution, are more permanently retained in the lattice of compounds with more stable chemical bonds [55].

The deviation from the general rule (of the ratio v_0/v_n increasing with lattice energy) shown by KI and KBr crystals at $\sigma \geq 0.006$ is ascribed to transition from the diffusion-kinetic dissolution regime to the diffusion-limited regime.

For each ion of a compound it is possible to select dissolution conditions and a solvent such that the parameters of the dissolution process (e.g. the rate of dissolution) are

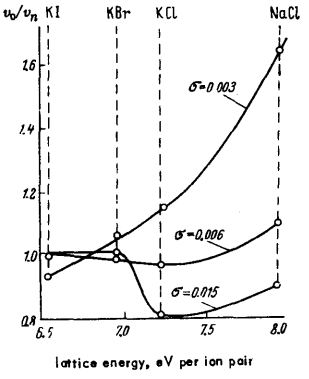


Fig. 5. Ratio of the linear dissolution rate v_0 of an irradiated (100) face to the rate of dissolution of a non-irradiated (100) face at different values of the relative undersaturation, σ, for crystals of different chemical composition after irradiation with 10^5 rad of 8 keV X-rays.

† Presumably the author means: The rate of dissolution *should be* lowest on the (110) face which has the *lower* density of ions compared with (100) but on the other hand the bonds between the ions on the (100) face are the strongest (Ed. of Translation).

sensitive to external interactions (e.g. to irradiation [55]). Thus, the linear rate of dissolution under specific conditions is a measure of the radiation stability of an ionic compound. Irradiation increases the density of defects in the material, loosens its structure, and increases the rate of dissolution. These effects are more marked in compounds of relatively high bond energy, since these can store radiation effects more successfully. High-energy compounds undergo changes in properties after irradiation because of the rapid annealing of radiation-induced defects. It can be assumed that the density of radiation defects will be greater in compounds with a lower bond energy, and that their properties will show relatively greater changes than those of compounds with a higher lattice energy.

Hence, it is important to investigate the dissolution mechanism and the characteristics of the process during irradiation of the solid to be dissolved.

The dependence of the time [sic], rate of melting, and rate of evaporation of a solid upon temperature is of scientific interest in the description of radiation damage (thermal spike), of the thermodynamics and theory of the solid state, and of the thermal decomposition of solids, etc.

The rate of thermal disintegration of a solid varies with experimental conditions, pressure, dose of radiation, and also with the structure of the solid (including structural defects).

The temperature dependence of the rate of evaporation v_{ev} of a solid in a vacuum is given by the expression

$$\log v_{ev} = A_1 - B_1/T, \quad (5)$$

where A_1 and B_1 are constants, and T (°K) is the evaporation temperature, or

$$v_{ev} = v_0 \exp(-E/RT)$$

where E is the heat of evaporation and R is the gas constant.

The temperature dependence of the vapour pressure P of metal oxides and of alkali metal halides is described by the approximate formula

$$\log P = A - \frac{B}{T} \quad (6)$$

where A and B are constants [57,58].

At higher temperatures the rate of evaporation increases, and the evaporation time τ decreases exponentially; the effect is analogous to an increase of stress during mechanical fracture.

The temperature dependence of the vapour pressure and the heats of evaporation of NaCl, KCl, KBr, and KI have been measured in the pressure range 10^{-1}–10^{-7} mmHg by the surface ionisation method. The heat of evaporation and the entropy were calculated from the results. The heat of evaporation and entropy for a temperature of 298° were also evaluated [58].

Fig. 6 shows graphs of $\log P = f(1/T)$. In the temperature range 1000–600°K the vapour pressure P (and therefore also the rate of evaporation) increase exponentially with specimen temperature.

The heat of evaporation of a substance and the entropy of solid compounds increase when the temperature is raised [59]. An increase of lattice energy also raises the heat of evaporation, lowers the entropy of the solid, and raises the entropy of the vapour. The vapour pressure and the rate

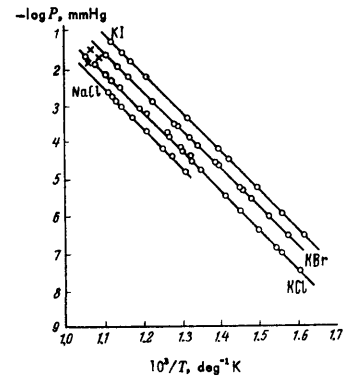


Fig. 6. Variation of $\log P$ with $1/T$. [57]

of evaporation of single crystals in a vacuum increase exponentially with temperature [59]. The evaporation coefficient, defined as the rate of evaporation from 1 cm² in 1 s divided by the rate of molecular collisions from the saturated vapour on 1 cm² in 1 s at the same temperature, is independent of temperature over a certain interval.

The higher the evaporation coefficient, the greater is the number of molecules evaporating from the surface and the weaker is the bond between particles.

At elevated temperatures the heat of evaporation decreases somewhat. Because of the different in the rates of evaporation from different crystal faces, stepped and mosaic structures are found after evaporation.

A similar behaviour is observed in tension: as the stress σ is increased, the heat of activation of the rupture process decreases according to the equation $U = U_0 - \gamma\sigma$, and the rate of tensile deformation increases exponentially [59].

The rate of evaporation of molybdenum and tungsten in a vacuum is increased by 80% or more on applying a field of 10^6 V cm^{-1}. The effect of strong electric fields (10^6 V cm^{-1}) on the rate of evaporation of the alkali metals is not yet known.

The evaporation of metals, oxides, and alkali metal halides in a vacuum and the mechanical failure of these materials show the same type of behaviour. As the driving force (temperature or tensile stress) increases, the rate of breakdown increases exponentially and the time of breakdown correspondingly decreases. Temperature increase lowers the heat of activation for evaporation and also the heat of activation of the process of failure in tension; the formation energy of the breakdown process decreases with increase of excess stress [59].

VI. SEMICONDUCTOR (ELECTRON–HOLE) PROPERTIES OF IONIC CRYSTALS AND THEIR CHEMICAL COMPOSITION

The electronic properties and other characteristics of crystals show a regular dependence on the lattice energy. The electronic properties can be discussed by treating the crystal as a system of interacting ions. We shall define the electronic levels in the isolated atoms by taking the energy of a free electron at rest in a vacuum as zero. The lowest unoccupied level of a free Na ion, corresponding to

the 3*s* state, is located below the zero level by an amount equal to the ionisation energy of 5.12 eV. The highest occupied level for the Cl^- ion is a 3*p* level, located below the vacuum level by an amount equal to the electron affinity of the Cl atom (4 eV).

Thus, the free 3*s* level lies below the occupied 3*p* level by 1.12 eV. As the free Na^+ and Cl^- ions are brought closer together, and the fraction of the chemical bond energy due to Coulombic interaction increases, the relative positions of the energy levels begin to change at a certain interionic distance, beyond which they become inverted. With further decrease of the interionic distance, the highest occupied 3*p* levels of the Cl^- ions are found to lie below the free 3*s* levels of Na^+.

When the distance between neighbouring ions reaches a value equal to the lattice parameter, by which time the wave functions of nearest ions of the same sign have begun to overlap, the discrete electronic levels of the atoms spread out into bands. The lattice parameter determines the band gap and the width of the bands. The levels corresponding to pairs of ions of the same kind overlap to form an energy band. The energy level diagram for electrons in crystals depends on the lattice parameter and on the energy spectrum of the lattice on the one hand, and on the electronic structure and levels of the atom on the other hand. For example, the lower (filled, or valence) band of an NaCl crystal is associated with the highest filled 3*p* levels of Cl^-, whilst the empty upper band of energy levels of the crystal corresponds to lowest unoccupied 3*s* levels of the Na^+ ions (Fig. 7).

The interaction between the atoms of a solid is reflected most strikingly by the energy conditions of the outer electrons of the atoms having the highest energy and exposed to the fields of neighbouring atoms situated at a distance a_0 apart.

The energy levels of the inner electrons for $r \leqslant a_0$ either do not split at all (1*s*) or split very slightly (2*s*). In this sense the crystal can be treated as a giant molecule, consisting of a large number of atoms and having the system of energy levels described above. The inner electrons of these atoms behave almost as though the atoms were isolated, whilst the outer electrons belong to the whole molecule-crystal. The energy of the electrons can lie within the regions shown hatched in Fig. 7 (the energy bands).

The valence electrons in atoms have several allowed levels, and therefore several bands of allowed electron energies are usually formed in crystals. The width of the forbidden energy gap is comparable to that of the allowed d bands. As the lattice energy decreases in Fig. 7, the width of the allowed energy bands increases and that of the forbidden gap decreases.

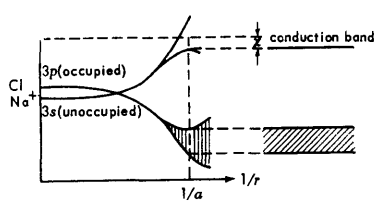


Fig. 7. Splitting of the different atomic levels under the influence of the field of neighbouring atoms.

The filling of the energy bands by electrons must satisfy Pauli's exclusion principle and at the same time minimise the energy of the system: hence, the lowest levels of the valence band are filled by electron pairs.

In real crystals the number of atoms, n, in 1 cm^3 is of the order of 10^{22}–10^{23}. The number of levels in each band must also be of the same order. The total width of the band is a few eV, and therefore the distance between adjacent levels is as low as $\sim 10^{-22}$ eV.

These effects give rise to some experimental observations interrelating the electron–hole transitions and properties in alkali metal halide crystals with the energetics of the ionic lattice in general, and with the chemical composition of a compound.

When the crystal lattice energy decreases, the width ΔE of the forbidden gap of electron energies also decreases, and the dielectric constant ϵ of the crystal increases. In alkali metal halides with *F*-centres the Mott relationship $\epsilon^{-2} \simeq \Delta E$, which was proposed for extrinsic semiconductors, is approximately obeyed.

The systematic increase of ϵ with decrease of lattice energy follows from the increasing polarisability of the anions on going from fluorides to iodides and of the cations on going from lithium to caesium, and also from the weakening of the Coulombic binding in the structure and from the increasing contribution of van der Waals interactions to the chemical bonding in these compounds. The dielectric properties and the stability deteriorate on going from lithium fluoride towards caesium iodide, as the ionic character of the chemical bond decreases.

The optical refractive index and the absorption coefficient over a wide range of radiation energies decrease as the lattice energy increases. The short-wave edge of the fundamental absorption and the maxima of the fundamental and additional absorptions in the infrared, visible, and ultraviolet regions of the spectrum for crystals activated by impurities are shifted towards shorter waves in this series of compounds by moving towards greater lattice energies whilst keeping the cation constant.

Some physical processes in crystals are not directly related to the lattice energy. For example, the scattering of phonons, photons, and high-energy particles at the atoms of which the crystal is composed. These processes are determined by the cross-section of the scattering centres, by the ionic radius, by the number of electrons, etc. As the radius of the ions in the compound increases the lattice energy decreases whilst photon, phonon, and particle scattering increases. Thus, a decrease in lattice energy is accompanied by enhanced absorption of radiation and of phonons, and by a decrease in the thermal conductivity and velocity of sound in the crystals.

This correlation allows us to extend to these properties the classification of the properties of ionic structures by means of a single parameter: the crystal lattice energy.

The properties of structures including other chemical bond types can likewise be classified in terms of a characteristic energy. Thus, in covalently bound semiconductors we note a correlation between various properties and the energy of atomisation or the heat of formation of the compound.

A classification of the properties of various glassy polymers can be based, as in the case of crystals, on the force binding together the structural units which give rise to the

polymer and into which the polymer breaks down when it decomposes. Increase of binding energy between the structural units of the glasses is accompanied by an increase in the temperature and heat of the glass transition, and of the thermal, mechanical, and chemical stability of the glass, as well as by a decrease in the loss angle and the electrical conductivity, and by a shift of the region of anomalous dispersion of the dielectric constant and of the losses towards higher temperatures.

The stability of solids towards radiation varies with chemical bond type. Chemical bonds can be placed in the following order of decreasing stability towards the action of ionising radiation: metallic, ionic, covalent, and (the least stable) molecular.

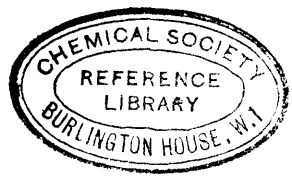
The available fund of experimental data allows us correctly to evaluate changes in the properties of compounds due to changes in chemical composition, and to arrive at a general picture of the rules which determine the influence of the chemical bond in a solid on the properties of the solid.

The classification of compounds on the basis of the chemical bond can give guidance in the search for new dielectrics and semiconductors, and in the determination of their properties. It may be less complicated to treat the properties of materials in terms of the chemical bond than to calculate them on the basis of band theory.

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ORIENTATION OF NUCLEOPHILIC ATTACK AT AN ACTIVATED DOUBLE BOND

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I. INTRODUCTION

An explanation for the regularities in cyanoethylation and condensation with $\alpha\beta$-unsaturated carbonyl-containing compounds (a particular type of which is known as the Michael condensation) has been sought frequently since the time they were discovered up to the present (see earlier reviews [1-4]). The investigators were interested in a simple and cheap path of synthesis for compounds of the most varied types, many of which became available even on an industrial scale.

The main condition for the successful use of ethylene compounds in these reactions is the presence of electron-acceptor groups which activate the double bond. However, the problems of a detailed study of the influence of electron-acceptor groups on the condensation from a quantitative standpoint received attention comparatively recently. The influence on the mechanism and rate of reaction of the introduction in series with the alkene bond of additional electron-acceptor groups and of their nature has also been little studied, although even now it is clear that this influence is undoubtedly great, as the example of tetracyanoethylene has shown. The latter, as is well known, not only reacts readily with nucleophilic reagents, forming addition and substitution products, but is also the strongest of the known π-acids, capable of giving a stable anion-radical, isolated in the form of salts with various cations [5,6].

In the present brief review an attempt is made to generalise some of the properties of $\alpha\beta$-substituted ethylene systems in which the double bond is under the inconsistent action of two electron-acceptor groups. Such systems can be symmetrical (identical electron-acceptor groups) or unsymmetrical (different groups), the interest being greatest in unsaturated compounds with electron-acceptor groups conjugated with the double bond. An explanation of the regularity in the direction of the attack of the nucleophilic agent for unsymmetrical $\alpha\beta$-diactivated ethylenes is also a subject of this review.

These problems are mainly considered by the example of the compounds RCOCH=CHX, where X is CN, CO_2R, NO_2, SO_2Ar, COAr, etc. In connection with this in the present review the preparation and reactivity of compounds of this type will receive most attention.

II. MECHANISM OF NUCLEOPHILIC REACTIONS OF AN ETHYLENIC BOND ACTIVATED BY ELECTRON-ACCEPTOR GROUPS

The mechanism of the reaction of an activated double bond with nucleophilic reagents was predicted theoretically by Ingold [7] and confirmed experimentally by several authors [8-14]. According to this mechanism the rate-determining stage is the addition of the nucleophilic reagent to the β-carbon atom of the double bond relative to the electron-acceptor substituent, which can be written in general form:

$$X{-}CH{=}CH_2 + Z^- \underset{}{\overset{\text{slow}}{\rightleftharpoons}} X{-}\bar{C}H{-}CH_2{-}Z \overset{+H^+\ \text{fast}}{\rightleftharpoons} XCH_2CH_2Z.$$

The reaction rate is given by the equation:

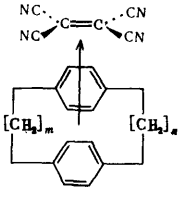
$$\frac{-d[XCH=CH_2]}{dt} = k[XCH=CH_2][Z^-].$$

The reactivity of monoactivated ethylenes with nucleophilic reagents is usually linked with the polarisation of the double bond[15] in these compounds, or, what is the same thing, with the presence of an appreciable positive charge on the β carbon atom of the double bond. From this standpoint the high reactivity (see Table 1) of the $\alpha\beta$-substituted† ethylenes of the *trans*-series is astonishing since the double bond in these compounds should be polarised comparatively weakly, as can be judged from the low intensity of the absorption band of the double bond in the infrared spectrum and the high intensity in the Raman spectrum[16].

The available information on the kinetics of the reaction of monosubstituted and $\alpha\beta$-disubstituted ethylenes, although meagre, allows some comparisons to be drawn. Table 1 gives data on the kinetics of the addition of methanol to an activated double bond, which show that the reaction rate is much greater than that for disubstituted ethylenes.

In this connection it is desirable to consider the molecule diagrams calculated by Shvarts[20] by the molecular orbital method for five cyano-substituted ethylenes. Table 2 gives some data from these calculations.

In examining these diagrams the positive charges on the ethylenic carbon atoms and the values of the energies of the lower vacant orbitals must be compared. Clearly the double bond is most polarised in the unsymmetrical compounds *1* and *2* (see Table 2). In these instances a considerable positive charge is concentrated on the β-carbon atoms in relation to the electron-acceptor groups. In compounds *3* and *5* there is no polarisation of the double bond (there is a small positive charge on both ethylene carbon atoms), but the level of the first vacant orbital lies considerably below that for *1* and *2*. This difference appears distinctly in the disubstituted alkenes *2* and *3*, the first of which is characterised by a strongly polarised double bond with the maximal value of the positive charge on all five cyano-substituents of the ethylenes and a higher level of the energy of the lower vacant orbital of the last four. An especially low energy level was calculated for tetracyanoethylene, in which it is close to the energy of the atomic orbital. Hence it can be seen that the accumulation of cyano-groups around the double bond lowers the energy of the first vacant orbital. This agrees well with the ability of tetracyanoethylene to form π-complexes and to give radical-anions by accepting one electron[5,6]. We note that π-π-complexes of tetracyanoethylene with *para*-cyclophanes are so stable that they could be isolated in the crystalline state[22].



orange for $m = n = 4$; red for $m = n = 6$, red-black for $m = 3$, $n = 4$.

Rather stable π-complexes are also formed by $\alpha\beta$-disubstituted ethylenes. According to Merrifield and Phillips[23], who studied complexes of maleic anhydride and *p*-quinone with pyrene (CH_2Cl_2, 22°) spectrophotometrically, the equilibrium constants for the formation of the complexes are 17.6 and 14.4 respectively. For tetracyanoethylene with the same π-base the constant is 29.5.

At the same time α- and $\alpha\alpha$-substituted ethylenes should show a very weak tendency to π-complex formation. Actually, even methylenemalononitrile forms a very weak complex with anthracene (benzene, 23°), the equilibrium constant for the formation of the complex being close to zero[24].

Unfortunately, the necessary quantitative data on the reactions of these compounds with nucleophilic reagents do not exist at present, so strict comparison with calculated data is impossible. Such comparisons would be especially interesting for methylenemalononitrile and fumarodinitrile. However, the difference in the positive charges and energy levels of the first vacant orbitals for the two types of substituted ethylenes (α and $\alpha\alpha$, or $\alpha\beta$ and $\alpha\alpha\beta\beta$) suggests that their reactions with nucleophilic reagents may have some differences in mechanism.

A possible hypothesis is that a not inconsiderable part (possibly the main part) in the mechanism of the $\alpha\beta$- and $\alpha\alpha\beta\beta$-substituted double bond is played by the ability to form π-complexes which subsequently rearrange into σ-complexes and then into the final product.

The correctness of this suggestion is confirmed by a series of experimental results. Actually tetracyanoethylene[5,6], tricyanovinyl chloride[25], dicyanobis(ethoxycarbonyl)ethylene[26], maleic anhydride[23], and esters of fumaric acid[27-29] have been separately shown to be capable of

TABLE 1. Data on the reaction kinetics for the addition of methanol to an activated double bond.

Alkene	K_{25}, litre mole^{-1} min^{-1}	Activation parameters
trans-$C_6H_5COCH{=}CHCN$[17]	425 (25°)	ΔE=13.5±1.3 kcal mole^{-1} ΔS=−11 e.u.
trans-$C_6H_5COCH{=}CHCOC_6H_5$[18]	182 (25°)	
$CH_2{=}CHCN$[13]	0.722 (25°)	ΔE=18.7 kcal mole^{-1} ΔS=−7.2 e.u.
$CH_2{=}CHCOCH_3$[19]	23.3 (19°)	

TABLE 2. Calculation of the molecular orbitals of cyano-substituted ethylenes*

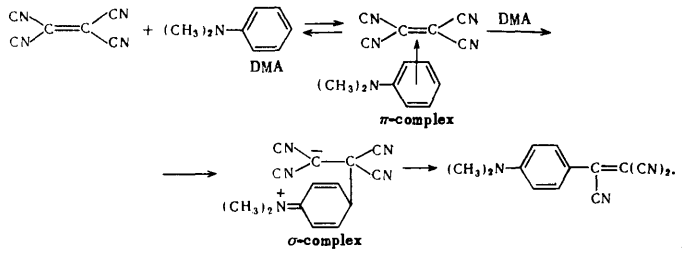
No.	Skeleton and charges on the carbon atoms of the double bond**	Energy of the lowest vacant orbital	Order of the ethylenic bond
1	−0.016 / +0.106	α−0.487β	1.886
2	−0.024 / +0.184	α−0.382β	1.802
3	+0.056 / +0.056	α−0.241β	1.784
4	+0.030 / +0.106	α−0.148β	1.704
5	+0.062 / +0.062	α−0.058β	1.638

* This table gives data calculated using Pullman and Pullman's parameters[21]

** The black circles denote CN groups, the lines C–H bonds.

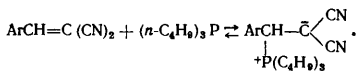
† In speaking of substituted ethylenes we will be thinking of ethylenes containing electron-acceptor substituents as well as the double bond.

forming π-complexes and of reacting with nucleophilic reagents. Rappoport and coworkers [30] have experimentally confirmed the formation of a π-complex which is an intermediate in the reaction of tetracyanoethylene with dimethylaniline. On investigating this reaction spectrophotometrically they found the rapid and reversible formation of a π-complex (K_{equil} = 15 litre mole^{-1}), which, they think, is converted into a σ-complex and then into the final product. This can be represented schematically:



Here it should be noted that a very low activation energy (5.7 kcal mole^{-1}) is found for the π-complex → σ-complex stage. Foster and Hanson suggested a similar mechanism for the reaction of tetracyanoethylene with indole [31].

On the other hand, of the α- and $\alpha\alpha$-substituted ethylenes, as noted above, even methylenemalononitrile forms a weak complex. In this connection it is interesting to consider the reaction of arylmethylenemalononitriles with tributylphosphine. In a spectrophotometric investigation of the kinetics of these reactions Rappoport and Gertler [32] observed the direct conversion of these compounds into an addition compound, having, according to the infrared spectra, the structure of a bipolar ion, which corresponds to the σ-complex:

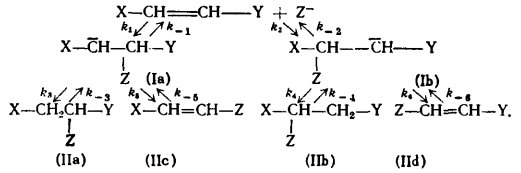


It was found that the addition product readily dissociates into the initial components. The authors did not observe any intermediate products within the sensitivity limits of the method.

Hence, on the basis of the above evidence it seems logical to suggest that the observed increase in reaction rate with methanol for $\alpha\beta$-disubstituted ethylenes in comparison with monosubstituted ones (see Table 1) can be due to the reaction with the disubstituted ethylenes proceeding through the intermediate formation of a π-complex.

III. ORIENTATION OF NUCLEOPHILIC ATTACK AT THE DOUBLE BOND OF THE X–CH=CH–Y SYSTEM

When ethylenes unsymmetrically substituted at each side react with nucleophilic reagents the orientation of the nucleophilic attack must be determined. The scheme of reaction of nucleophilic reagents with compounds of the type XCH=CH–Y, where X and Y are electron-acceptor groups, can be represented in the general form as follows:



In this, there are different probabilities of the formation of two carbanions (Ia) and (Ib). Kinetic investigations of reactions of this type undertaken by various authors [18] and by us [17,33] agree with these suggestions‡.

The stabilisation path of these carbanions will depend on several factors and above all on the nature of X and Y, on the nature of the nucleophilic substance, and on the surrounding medium. The stabilisation directions most frequently realised are§: (1) the addition of a proton or any positive species, as a result of which addition products (IIa) and (IIb) are formed; (2) ejection of an anion or neutral molecule and formation of substitution products (IIc) and (IId); (3) hydrolytic breakdown when the nucleophilic reagent is the OH^- ion. Naturally, the first stabilisation path of carbanions (Ia) and (Ib) predominates in systems where X and Y are electron-acceptor groups incapable of readily leaving in the form of anions (for example, RCO–, COOR). On the other hand, for X and Y which are easily removed in the form of stable anions (NO_2, halogens) the second path is possible. Naturally, for some examples of systems which we will consider mixed stabilisation of carbanions can occur (for example, where X is a group readily leaving as an anion and Y is not.

Let us consider additions and their energetic profile (Fig. 1), that is, that part of the general scheme by which products (IIa) and (IIb) are formed. According to the theory of the transition state, the ratio of the amounts of two kinetically controlled reaction products (P) formed from a single initial substance depends solely on the difference between the free energy levels of the two transition states and is not connected with the free energy level of the principal state (it is suggested that the reaction includes

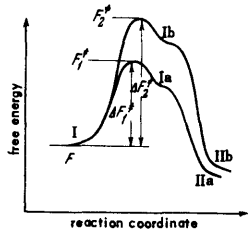
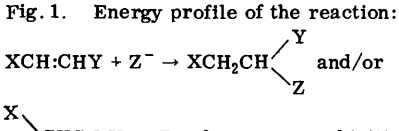
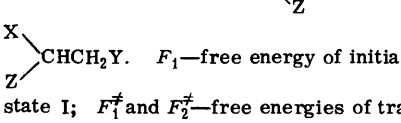


Fig. 1. Energy profile of the reaction:



and/or



F_1—free energy of initial state I; $F_1^{\neq}$ and $F_2^{\neq}$—free energies of transition states leading to the carbanions (Ia) and (Ib).

‡ The kinetic data also do not contradict the intermediate formation of a π-complex.

§ In the present work we shall consider only some of the possible stabilisation paths. For a detailed discussion of this problem see the paper of Patai and Rappoport [34].

the same kinetic expressions for the formation of both products)

$$P = \frac{k_1}{k_2} = e^{\frac{F_1^{\neq} - F_2^{\neq}}{RT}}.$$

In our particular instance the direction of attack of the nucleophile will be determined by the ratio k_1/k_2, and evidently to form a judgement about it the transition states leading to the carbanions (Ia) and (Ib) must be considered and an attempt made to evaluate their relative free energies $F_1^{\neq}$ and $F_2^{\neq}$. According to Hammond's hypothesis [35] the transition states can suggest by their structure the final products of a given stage, that is, the carbanions (Ia) and (Ib)¶ in our example and in the first rough approximation can be limited to comparison of the relative stability of the carbanions themselves, $X\overline{C}H-CHYZ$ (Ia) and $XZCH-\overline{C}HY$ (Ib) and this, in turn, for lack of other data, has to be judged from dissociation constants or from the rate constants for deuterium exchange of substituted methanes $X-CH_3$ and $Y-CH_3$. Here it is suggested that the stability of the anions depends primarily on the capability of the group directly adjoining the anionic centre to delocalisation of the negative charge. Such an approach is of course a considerable simplification, above all because it starts from these assumptions: the transition states which are formed either by the addition of negatively charged species to the double bond, or as a result of the dissociation of C–H bonds in saturated hydrocarbons, can be comparable in their structure†, that is:

$$X-CH=CH-Y+Z^- \rightleftarrows X-\overset{\overset{|}{Z}}{\overline{C}H}-CH-Y \rightleftarrows X-CH_2-\underset{\underset{|}{Z}}{CH}-Y.$$

Moreover, this approach makes no allowance whatsoever for the fact that steric factors for groups ZYCH in (Ia) and ZXCH in (Ib) and solvents (especially strongly solvating anions) can have a significant influence on the formation of carbanions. Furthermore, the possibility of interaction between the groups themselves which enter into the carbanion and the formation of cyclic transition states can be of great importance. However, this approach can be useful to a certain extent since it is valid for many reactions, which will be considered below.

It is noteworthy that for most substitutions where the heterolysis of the C–X or C–Y bond in the stabilisation of carbanions (Ia) and (Ib)—with the formation of the products (IIc) and (IId)—takes place very readily (where the group leaving is a halogen or NO_2), the energy profile can relate solely to what has been discussed. However, a more complex example is presented by substitutions in which the heterolysis of the C–X(Y) bond proceeds slowly. Fig. 2 shows the generalised picture of the energy profile for such reactions.

There are several experimental facts which agree with the above ideas on the orientation of attack by a nucleophile at an ethylenic double bond activated at each side. We will restrict discussion mainly to those instances for which the dissociation constants of the corresponding substituted methanes or the rates of their deutero-exchange are known.

¶ According to the results of most of the kinetic investigations, the addition of nucleophilic reagents at an activated double bond leading to the formation of carbanions is the limiting stage of the process [7–14]. The rapid second stage of protonation proceeds in practice with a low activation energy [36].

† Possibly a more complete introduction to the transition state in these examples can be given by a study of the secondary α-isotopic effect [37,38].

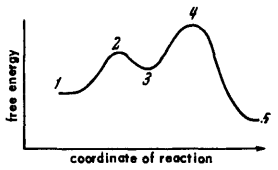


Fig. 2. Energy profile of the reaction: XCH=CHY + Z^- → XCH=CHZ and/or ZCH=CHY where the heterolysis of the C–X(Y) bond is slow.
1) Initial state; 2) transition state leading to carbanion 3; 4) transition state of heterolysis of the C–X(Y) bond; 5) final state.

On comparing the dissociation constants of nitromethane ($K_{CH_3NO_2} = 6 \times 10^{-11}$) [39] and acetic acid ($K_{CH_3CO_2H} = 10^{-24}$) [39] (see Table 3), it can be predicted that β-nitroacrylic acid will add on nucleophilic reagents in the following manner:

$$NO_2CH=CHCOOH + HZ \rightarrow NO_2CH_2\underset{\underset{|}{Z}}{CH}COOH.$$

In fact, Shechter and coworkers [42] have shown that this acid adds on methanol and water with the formation of products of this structure. It is important to note that the addition of methanol proceeds very easily even in the absence of basic catalysts.

On studying the deuterium exchange of *cis*- and *trans*-arylsulphonylacrylic acids in D_2O–NaOD medium by NMR spectra, Montanari and coworkers [43] found that the β-H is exchanged first, then the α-H, and addition products with deuterium oxide (III) and (IV) are formed:

$$ArSO_2CH=CHCOOH \rightarrow ArSO_2CD=CHCOOH \rightarrow ArSO_2CD=CDCOOH$$
$$\downarrow D_2O \qquad \downarrow D_2O$$
$$ArSO_2CD_2\underset{\underset{|}{OD}}{CH}COOH \qquad ArSO_2CD_2\underset{\underset{|}{OD}}{CD}COOH.$$
$$\text{(III) } 20\% \qquad \text{(IV) } 80\%$$

In H_2O–NaOH solution (III) exchanges all the deuterium atoms for hydrogen, but (IV) under the same conditions retains one deuterium atom, which rules out alternative structures for the β-hydroxy-acids in which after the exchange one or two deuterium atoms respectively should remain. Although in the sulphonyl-substituted methane series the dissociation constant is known only for dimethylsulphone ($K_{CH_3SO_2CH_3} = 10^{-23}$) [39] there will be no great error in taking the dissociation constant for $CH_3SO_2C_6H_5$ to be close to this value.

TABLE 3. Dissociation constants for substituted methanes.

Substituted methane	Dissociation constant of the C–H bond	Reference	Substituted methane	Dissociation constant of the C–H bond	Reference
CH_3NO_2	$6.1 \cdot 10^{-11}$	39	$(CF_3)_2CFH$	10^{-20}	40
CH_3COCH_2COOR	$2.1 \cdot 10^{-11}$	39	$CH_3SO_2CH_3$	10^{-23}	39
$(CF_3)_3CH$	10^{-11}	40	CH_3COOH *	10^{-24}	39
$CH_2(CN)_2$	$6.5 \cdot 10^{-12}$	39	$CH_3COOC_2H_5$	$10^{-24.5}$	39
$CH_2(COOC_2H_5)_2$	$5 \cdot 10^{-14}$	39	CH_3CN	10^{-25}	39
$C_6H_5COCH_3$	10^{-19}	41	CH_3CONH_2 *	10^{-25}	39
CH_3COCH_3	10^{-20}	39	$CF_3(CF_2)_2CF_2H$	10^{-30}	40

* Here, naturally we refer to constants for dissociation with the formation of the anions $^-CH_2CO_2H$ and $^-CH_2CONH_2$ and not $CH_3CO_2^-$ and $CH_3\overline{CONH}$.

Trichloromethylnitroethylene[3,3,3-trichloro-1-nitroprop-1-ene] also exhibits an extremely electrophilic double bond and with nucleophilic reagents it gives addition products [44-49] of the expected structure:

$$CCl_3CH{=}CHNO_2 + HZ \rightarrow CCl_3\underset{\underset{Z}{|}}{C}HCH_2NO_2$$

where HZ = amines, alcohols.

By the action of hydrogen chloride upon it, Dornow and coworkers [50] obtained an α-chloro-oxime, for the formation of which they proposed the following mechanism:

$$CCl_3CH{=}CHNO_2 + HCl \longrightarrow CCl_3\underset{\underset{Cl}{|}}{C}HCH_2NO_2 \longrightarrow$$

$$\longrightarrow CCl_3{-}\underset{\underset{Cl}{|}}{C}H{-}CH{=}\overset{+}{N}\begin{matrix}O^-\\ \diagdown\\ \diagup\\ OH\end{matrix} \xrightarrow{HCl} CCl_3CHCl{-}CH{=}NOH.$$

Perfluoroalkylnitroethylenes react‡ in an analogous fashion [51,52]:

$$R_fCH{=}CHNO_2 + HZ \longrightarrow R_f\underset{\underset{Z}{|}}{C}HCH_2NO_2,$$

where $R_f = CF_3$, C_3F_7, and HZ = $CH_2(CO_2R)_2$, C_2H_5OH, p-$NH_2C_6H_4CO_2H$, CH_3NO_2, or RMgX.

By studying the addition of water and ammonia to β-trifluoromethylacrylic acid and its derivative (V), Walborsky and coworkers [53,54] explained their results by the ability to stabilise the neighbouring anionic centre in the transition state being less for the CF_3 group than for the CO_2H, CO_2R, or $CONH_2$ groups. McBee and coworkers carried out an analogous work [55]:

$$CF_3CH{=}CHCOOR + HZ \longrightarrow CF_3\underset{\underset{Z}{|}}{C}HCH_2COOR.$$

(V)

Knunyants and Cheburkov [56] and McBee and coworkers [57] found that the methyl ester of 3-methyl-4,4,4-trifluorocrotonic acid (VI) adds on nucleophilic reagents as follows:

$$\begin{matrix}F_3C\\ \diagdown\\ H_3C\end{matrix}\!\!>C{=}CHCOOCH_3 + HZ \longrightarrow \begin{matrix}F_3C\\ \diagdown\\ H_3C\end{matrix}\!\!>\underset{\underset{Z}{|}}{C}{-}CH_2COOCH_3.$$

(VI)

As Table 3 shows, the attachment of CF_3 groups sharply raises the acidity of the hydrogen atoms in the α-position. In accordance with this ethyl $\beta\beta$-bis(trifluoromethyl)acrylate (VII) reacts according to the scheme [58]:

$$\begin{matrix}F_3C\\ \diagdown\\ F_3C\end{matrix}\!\!>C{=}CHCOOR + HZ \longrightarrow \begin{matrix}F_3C\\ \diagdown\\ F_3C\end{matrix}\!\!>\underset{\underset{Z}{|}}{C}H{-}CHCOOR.$$

(VII)

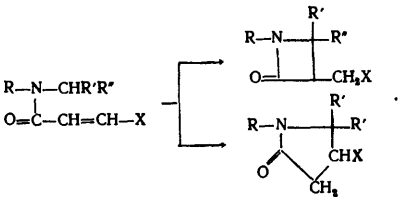
On determining the relative rate of formation of anions from deuterohaloforms, Hine and coworkers [59] found that in their ability to accelerate this reaction the halogens are arranged in the following order: I ~ Br > Cl > F. Slaugh and Bergman [60] came to similar conclusions in studying the kinetics of deuterium exchange in haloforms. This suggests that fluorine atoms stabilise neighbouring anionic centres worse than the other halogens. In this connection it is interesting to note that dichlorodifluoroethylene and chlorotrifluoroethylene add on nucleophilic reagents thus [61-63]:

$$CF_2{=}CCl_2 + HZ \rightarrow ZF_2C{-}CHCl_2$$
$$CF_2{=}CFCl + HZ \rightarrow ZF_2C{-}CHClF\ .$$

The following results evidently also fit into the framework of the rule being considered [64]:

$$(AlkO)_2\overset{O}{P}{-}CH{=}CHCOOR + H{-}\overset{O}{P}(OAlk)_2 \rightarrow ROCOCH_2CH\left[\overset{O}{P}(OAlk)_2\right]_2.$$

Bose and coworkers [65] observed an interesting dependence of cyclisation upon the nature of substituent X in β-substituted acrylamides. They found that in cyclisation instead of the γ-lactams usually obtained, β-lactams are formed when X = CO_2R or p-$NO_2C_6H_4$:



The most extensive study of the orientation of the addition of nucleophilic reagents was made for the RCOCH=CHX system, where X represents an electron-acceptor group; therefore we will consider these examples in somewhat greater detail. It is noteworthy that there is a general method of making most of these compounds, based on the reaction known as β-ketovinylation§.

β-Ketovinylation can be effected in two ways, which differ in principle. The first is based on nucleophilic substitutions, mainly in β-chlorovinyl ketones¶ and in β-acylvinyltrimethylammonium salts. In the second, which has been comparatively little developed, nucleophilic addition to the triple bond of ethynyl ketones is employed [73-75]:

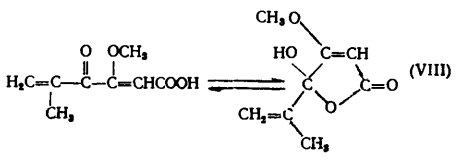
$$\begin{matrix}RCOCH{=}CHCl & [\text{or } \overset{+}{N}(CH_3)_3] & \xrightarrow{X^-}\\ RCOC{\equiv}CH & \xrightarrow{HX} & \end{matrix} \rightarrow RCOCH{=}CHX\ .$$

Note that as the present authors have shown in various papers it is best to use β-acylvinyltrimethylammonium salts for the ketovinylation of anions [76-80].

The chemistry of the β-acylacrylic acids† started to develop extremely rapidly after it had been observed that antibiotic action was exhibited by a series of compounds containing the grouping

$$-CO-\underset{\underset{|}{}}{C}=C-COOH,$$

especially penicillic acid (VIII): [154]



(VIII)

‡ Andreades [40] gives $K = 10^{-30}$ for $CF_3[CF_2]_5CF_2H$. Evidently it can be assumed that the dissociation constants of CF_3CH_3 and $C_3F_7CH_3$ will be even smaller.

§ The term ketovinylation implies the introduction of the residue RCOCH=CH into the molecule. This term was proposed by Kochetkov [66].

¶ The chemistry of the β-chlorovinyl ketones has been presented in several reviews [66-71] and in a book [72].

† Preparation described elsewhere [81-153].

Since many authors thought that the antibiotic action of these compounds is based on the ability of easily adding on the active SH–, and possibly >NH, groups of bacterial enzymes, the β-acylacrylic acids and their derivatives were studied intensively in pharmacology. They were actually shown to be active against a series of gram-positive and gram-negative bacteria[93,95,144,155-159] and in some instances they showed fungicidal activity[94]. The nucleophilic reactions of the β-acylacrylic acids take place very readily and were investigated for a wide range of nucleophilic reagents. On comparison of the dissociation constants of acetophenone ($K_{C_6H_5COCH_3} = 10^{-19}$) [41] and of acetic acid, its amide, and esters ($K_{CH_3CO_2H} = 10^{-24}$, $K_{CH_3CONH_2} = 10^{-25}$, and $K_{CH_3CO_2R} = 10^{-24.5}$), [39] it can be suggested that addition products of the following structure are formed:

$$RCOCH{=}CHCOOR' + HZ \rightarrow RCOCH_2\underset{\displaystyle Z}{\underset{|}{C}}HCOOR\ .$$

Actually in most of the investigations‡ it was found that as a result of the reaction of the β-acylacrylic acids or their derivatives with nucleophilic reagents, α-substituted β-acylpropionic acids are formed. For example, even in the first work on the investigation of the properties of β-benzoylacrylic acid[168] it was shown that it readily adds on water, sodium cyanide, ammonia, aniline, hydrogen halides§, and that the general scheme of reaction can be represented as above. Sodium sulphite also adds on similarly[92,170].

Cromwell and coworkers[171,172] studied the reaction of methyl β-benzoylacrylate with primary and secondary amines:

$$C_6H_5COCH{=}CHCOOCH_3 + HNR_1R_2 \rightarrow C_6H_5COCH_2\underset{\displaystyle NR_1R_2}{\underset{|}{C}}HCOOCH_3.$$

The study of the various conversions of the reaction products and above all their reduction to α-amino-γ-phenylbutyric acids, showed that amines add on in the α position to the methoxycarbonyl group.

The reaction of β-aroylacrylic acids with ammonia proceeds in a similar manner[149,152,168,173]. The structure of the addition product of β-benzoylacrylic acid and ammonia:

$$ArCOCH{=}CHCOOH + NH_3 \rightarrow ArCOCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH$$

was shown by the yield of the known β-benzoyl-α-hydroxypropionic acid under the action of nitrous acid:

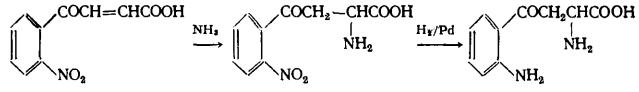
$$C_6H_5COCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH \xrightarrow{HNO_2} C_6H_5COCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOON\ .$$

‡ The work of a group of French authors[160-167] somewhat contradicts these results; the French workers ascribe to the products of the addition of ammonia and amines the structure of β-acyl-β-aminopropionic acids, without giving, in essence, any evidence in support of their structures.

It is curious that in their earliest work[168] these very investigators held a contrary opinion about the orientation of the addition of amines.

§ The addition of hydrogen halides to αβ-unsaturated ketones can be considered as the proton-catalysed addition of weak nucleophilic reagents—halide anions[169].

The ability of β-aroylacrylic acids to add on ammonia was used in several studies to make *dl*-kynurenine and some of its derivatives[81,149-153]:



It is known that *l*-kynurenine—a natural α-amino-acid—plays an important part in the genetic formation of pigments in insects[174] and is also the main product of the metabolism of tryptophan in the organism of mammals and micro-organisms[174,175]. Kynurenine was first synthesised by Butenandt[176,177], who also established its structure.

It was shown that β-benzoylacrylamide also readily adds on aniline[178]:

$$C_6H_5COCH{=}CHCONH_2 + NH_2C_6H_5 \rightarrow C_6H_5COCH_2\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}HCONH_2.$$

Bougault and Chabrier[179] investigated the reaction of β-benzoylacrylic acid with thiols and found that the orientation of nucleophilic attack is here the same as for amines

$$C_6H_5COCH{=}CHCOOH + RSH \rightarrow C_6H_5COCH_2\underset{\displaystyle SR}{\underset{|}{C}}HCOOH.$$

Additions of cysteine can also be classified as this type of reaction[95]. Reactions of β-aroylacrylic acids with alcohols have been somewhat less studied. Here reference can be made to the work of Lutz and Scott[180,181] and also to Rice's earlier paper[182], where it was assumed that methanol adds on in the α position to the carboxyl group:

$$ArCOCH{=}CHCOOH + CH_3OH \longrightarrow ArCOCH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}HCOOH.$$

It was found[166,168] that in acid medium water adds on to β-benzoylacrylic acid with the formation of β-benzoyl-α-hydroxypropionic acid:

$$C_6H_5COCH{=}CHCOOH + H_2O \xrightarrow[H^+]{} C_6H_5COCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH\ .$$

At the same time aqueous alkali solutions bring about hydrolytic splitting of the double bond[85,167,168,183,184]:

$$C_6H_5COCH{=}CHCOOH + H_2O \xrightarrow[OH^-]{} C_6H_5COCH_3 + CHOCOOH\ .$$

According to the generally accepted mechanism of similar reactions[185-189] the rate-limiting stage of the reaction is the addition of hydroxide ion to the double bond, as a result of which a carbanion (IX) is formed. The formation of acetophenone thus demonstrates that here the usual direction of nucleophilic attack is retained:

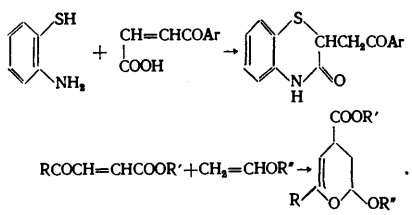
$$C_6H_5COCH{=}CHCOOR + OH^- \longrightarrow C_6H_5C\underset{\displaystyle OH}{\underset{|}{\bar{C}}}HCHCOOR \rightleftarrows$$

(IX)

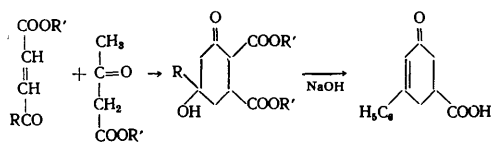
$$\rightleftarrows C_6H_5COCH_2\underset{\displaystyle O^-}{\underset{|}{C}}HCOOR \longrightarrow C_6H_5C\bar{O}H_2 + CHOCOOR.$$

$$\qquad\qquad\qquad

is known, and for many of these it is natural to postulate initial addition at the α-carbon atom of the double bond [193-194], for example:

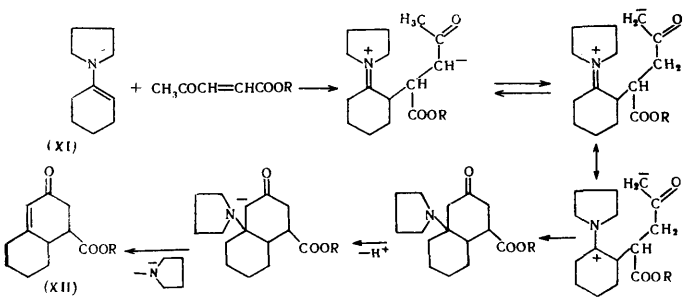


Julia and Bonnet [190] proposed to use the condensation of β-acylacrylic acids (or esters) with acetoacetic ester in the presence of basic catalysts for the synthesis of substituted cyclohexenones. It was shown, by the example of β-benzoylacrylic ester, that the reaction proceeds through an intermediate cyclic addition product (X), which under the action of alkali leads to a 3-substituted 5-carboxycyclohex-2-en-1-one. The ester of this acid is readily dehydrogenated into an ester of 3-hydroxy-5-phenylbenzoic acid, which also confirms its structure:

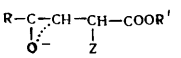


(X)

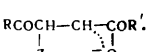
The diethylamide of acetoacetic ester reacts analogously [190]. In a brief communication Stork and Landesman [195] described the reaction of ethyl β-acetylacrylic acid with an enamine (XI), as a result of which a bicyclic product (XII) was isolated:



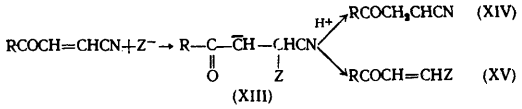
Hence all the known reactions of β-acylacrylic acids with nucleophilic reagents are characterised on the one hand by the ease with which they take place (apparently connected with the marked electron impoverishment of the ethylene bond in these compounds) and on the other by the invariable direction of attack by the nucleophile, which is probably explained by the stability of the carbanion of type



which is formed being greater than that of the carbanion



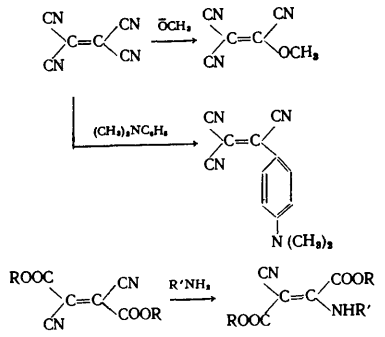
For β-cyanovinyl ketones [76] (the nitriles of β-acylacrylic acids) the expected direction of attack by the nucleophilic reagent:



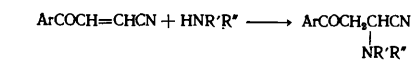
(XIII)

is the same as for the β-acylacrylic acids.

Let us remember that ($K_{C_6H_5COCH_3} = 10^{-19}$) [41] and ($K_{CH_3CN} = 10^{-25}$). [39] Actually in all the instances studied only one reaction product was observed in the reaction medium and this product contained the nucleophilic moiety in the β position to the carbonyl group, as was confirmed by thin-layer chromatography. However, unlike the β-acylacrylic acids, the intermediate carbanion (XIII) which is formed in attack by the nucleophile Z^- can be stabilised in two ways, giving addition product (XIV) as a result of protonation (Fig. 1 can represent the energy profile) and the substitution product (XV) as a result of possible heterolysis of the C–CN bond (energetic profile of Fig. 2). It is noteworthy that replacement of the CN group at an activated double bond has been observed repeatedly in the reactions of tetracyano-1,2-diethoxycarbonylethylene [5,196] and 1,2-dicyano-1,2-diethoxycarbonylethylene [197] with certain nucleophilic reagents:

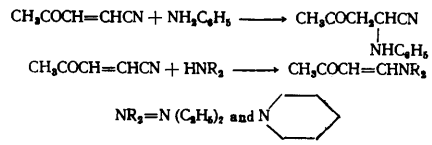


Nesmeyanov and Rybinskaya [178,198] showed that the reaction of β-cyanovinyl ketones with amines (primary and secondary) takes place very readily on simple mixing of the reagents in an appropriate solvent, as for β-acylacrylic acids. In this way aryl β-cyanovinyl ketones give an addition product in high yield. The method can serve as a preparative path for the synthesis of α-amino-γ-ketonitriles·

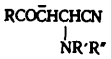


The structure of these compounds was shown by hydrolysis, which yielded known α-amino-β-benzoylpropionic acids.

However, methyl β-cyanovinyl ketone gives an addition product only with aniline [178], and the reaction is slower than for the aryl β-cyanovinyl ketones. Substitution products are formed with diethylamine and piperidine [198]:

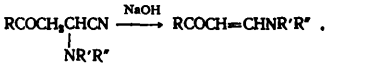


The latter is evidently explained by aliphatic amines being stronger bases than aniline, so that the equilibrium is more displaced towards the intermediate carbanion (XVI),

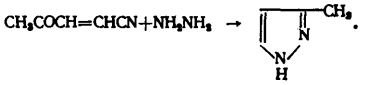


(XVI)

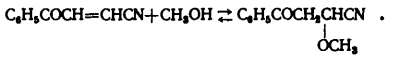
as a result of which the possibility of heterolysis of the C–CN bond is increased. It is therefore natural that the action of bases stronger than the amines (for example, alkalis) on the addition products should result in the loss of a molecule of hydrogen cyanide [178,198]:



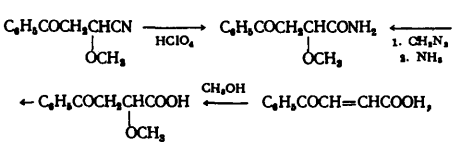
It is interesting to note that β-cyanovinyl methyl ketone, like β-chlorovinyl methyl ketone [199], gives 3-methylpyrazole with hydrazine:



Nesmeyanov and coworkers [17] showed that in the presence of basic catalysts *cis*- and *trans*-β-cyanovinyl phenyl ketones [200] add on methanol to form β-benzoyl-α-methoxypropionitrile:



This was hydrolysed by 70% perchloric acid to give the β-benzoyl-α-methoxypropionamide:

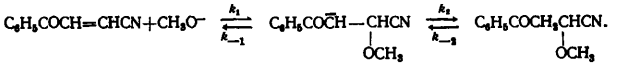


which was obtained by counter-synthesis from β-benzoylacrylic acid. Consequently the direction of the addition of methanol to β-cyanovinyl phenyl ketone is the same as to β-benzoylacrylic acid. The addition of methanol to *cis*- and *trans*-β-cyanovinyl phenyl ketones seemed a convenient method for the investigation of kinetics and mechanism [17]. Spectrophotometric studies of the kinetics showed that the reaction is reversible, but the equilibrium is strongly displaced to the side of the addition product and the equilibrium position is almost independent of the pH of the medium but dependent upon temperature (at 10° there is 90% addition, at 25°, 85%). It was found that the reaction is of first order in both *cis*- and *trans*-β-cyanovinyl phenyl ketones and first order in methoxide ion¶.

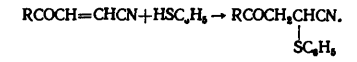
From a comparison of the second-order rate constants at 25°, k_1, *trans* = 425 litre mole^{-1} min^{-1} and k_1, *cis* = 260 litre mole^{-1} min^{-1} it is evident that there is a not very marked relation between the reaction rate and the geometrical isomerism in the β-cyanovinyl phenyl ketones.

¶ See Table 1 for the activation parameters.

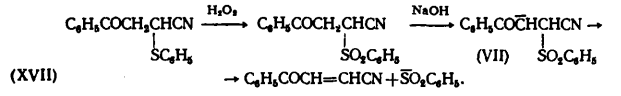
The experimental results agree with the reaction mechanism, which postulates a slow attack by the methoxide anion in the first stage with subsequent rapid protonation of the carbanion formed:



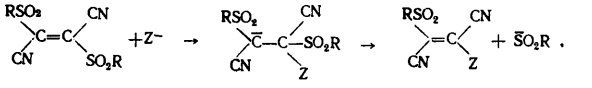
Alkyl and aryl β-cyanovinyl ketones add on thiophenol, the reaction being accelerated by the presence of bases, as a result of which β-acyl-α-phenylmercaptopropionitriles are formed in high yield [201]:



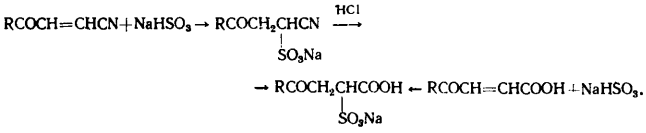
The structure was shown by the hydrolysis into the known β-aroyl-α-phenylmercaptopropionic acids. The β-acyl-α-phenylmercaptopropionitriles are oxidised by peroxide to the corresponding sulphones, which are more stable than the initial phenylmercapto-derivatives. It is interesting that when alkali acts on the latter there is an elimination of benzene sulphinic acid, which is evidently evidence that the heterolysis of the C–$SO_2C_6H_5$ bond in the carbanion (XVII) formed as intermediate is easier than the heterolysis of the C–CN bond:



Probably it is for the same reason that when 1,2-dicyano-1,2-disulphonylethylene reacts with nucleophilic reagents a sulphonyl group and not a nitrile group is replaced [202]:

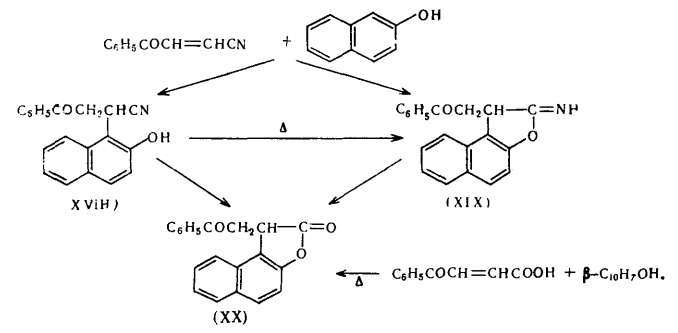


Aryl β-cyanovinyl ketones also add on sodium hydrogen sulphite very readily in aqueous alcoholic medium [176]. When the addition products are boiled with concentrated hydrochloric acid the monosodium salts of β-aroyl-α-carboxyethanesulphonic acids are formed, which can be obtained by direct synthesis from β-aroylacrylic acids [92,170]:

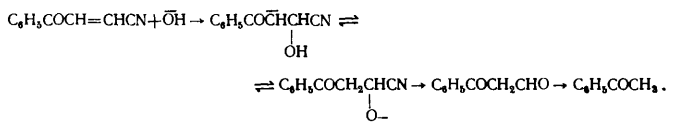


β-Cyanovinyl phenyl ketones react with 2-naphthol in the presence of catalytic quantities of calcium hydroxide [198]. When the reaction is carried out in 10 : 1 water–dioxan mixture in the cold in the presence of calcium hydroxide, β-benzoyl-α-(2-hydroxynaphthyl)propionitrile (XVIII) is formed. However, the same reaction at room temperature in 1 : 9 water–dioxan mixture with addition of catalytic amounts of calcium oxide gives a cyclic addition product, the imine of 1-*H*-1-phenacylnaphtho[2,1-*b*]furan-2-one (XIX). On hydrolysis with hydrochloric acid, (XVIII) and (XIX) are converted into 1-*H*-1-phenacylnaphtho[2,1-*b*]furan-2-one

(XX), which was also obtained by fusion of β-benzoylacrylic acid with 2-naphthol:

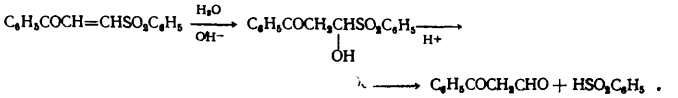


As might be expected, under the action of aqueous alkali β-cyanovinyl phenyl ketones decompose with the formation of acetophenone[78]:

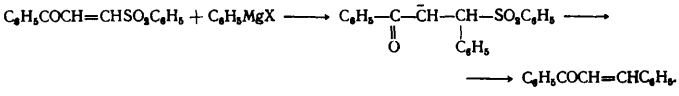


The addition of nucleophilic species in the β position to the carbonyl group is also characteristic for the αβ-unsaturated ketosulphones[73-75,80,203,204] $RCOCH{=}CHSO_2C_6H_5$ ($K_{C_6H_5COCH_3} = 10^{-19}$ and $K_{CH_3SO_2CH_3} = 10^{-23}$).[39,41] As already noted, there is a possibility of heterolysis of the C–SO_2R bond from the β position to a negatively charged atom in the intermediate carbanion. Therefore for αβ-unsaturated ketosulphones the formation of addition and substitution products is to be expected. However, the reactions of β-benzoylvinyl sulphone have only been investigated for a limited number of examples.

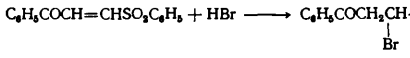
Kohler and Larsen[204] found that the addition of water is catalysed by bases. The addition product obtained decomposes into benzoylacetaldehyde and benzenesulphinic acid:



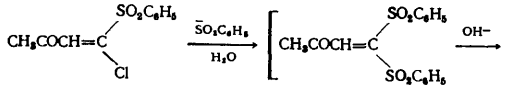
In the reaction with a Grignard reagent the main product is a chalcone[204]:

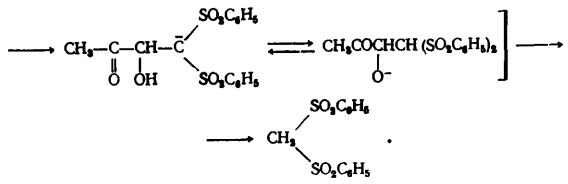


The same authors found that the addition product of hydrogen bromide has the structure of 2-benzoyl-1-bromoethyl phenyl sulphone[204]:

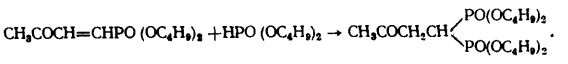


The following results[205] can evidently be classified as in agreement with the rule stated above (note that $K_{CH_2(SO_2CH_3)_2} = 10^{-14}$):[39]



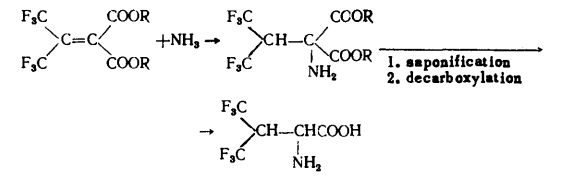


Note also the work of Kreutzkamp and Schindler[206], who showed that dibutyl 2-acetylvinylphosphonate adds on dibutyl phosphite to form tetrabutyl 2-acetylethane-1,1-diphosphonate:

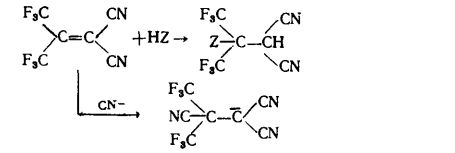


Hence the examples mentioned can serve as illustrations of the position stated above: that the direction of nucleophilic attack in XCH=CHY systems can be judged by comparison of the dissociation constants of the corresponding substituted methanes.

However, the above approach does not always fit the experimental facts. For example, it is inapplicable to ethylenic systems which contain several bulky substituents at the double bond, capable of delocalisation of the neighbouring anionic centre, mainly owing to the conjugation effect. As Ch'en and coworkers[207] showed, the reverse of the expected direction of attack of the nucleophile occurs for hexafluoroprop-2-ylidenemalonic ester with ammonia ($K_{(CF_3)_2CH_2} \simeq 10^{-20}$†, $K_{CH_2(CO_2R)_2} = 10^{-14}$).

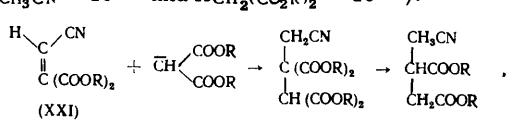


The structure of this product was convincingly demonstrated by conversion into hexafluorovaline, which was known already. At the same time, nucleophilic reagents add on in the expected direction to 1,1-dicyano-2,2-bis-(trifluoromethyl)ethylene, in which the ethoxycarbonyl groups have been replaced by more compact CN groups ($K_{CH_2(CN)_2} = 10^{-12}$).[39] As Middleton has shown[208] 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene reacts with aniline, water, and cyanide ion as follows:



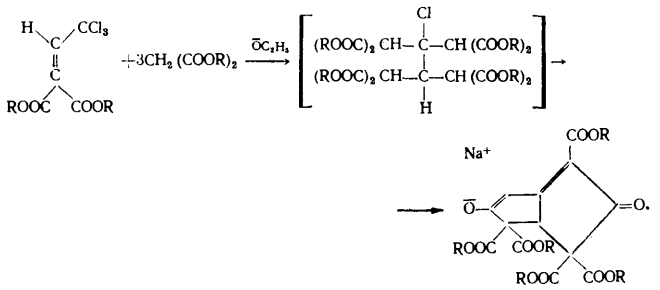
where Z = OH or NHC_6H_5.

Uchibayashi's results[209] also do not fit within the framework of the proposed hypothesis. He studied the reaction of cyanomethylenemalonic ester (XXI) with sodiomalonic ester ($K_{CH_3CN} = 10^{-25}$ and $K_{CH_2(CO_2R)_2} = 10^{-14}$):[39]

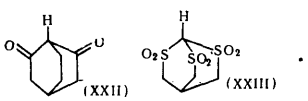


† Andreades[40] gives $K = 10^{-20}$ for $(CF_3)_2CFH$; it can be assumed that $K_{(CF_3)_2CH_2}$ will be even less.

However, the replacement in this example of the cyano-group by the CCl_3 group‡, which is considerably less capable of stabilising a negative charge, leads to a product with the expected orientation of attack by a nucleophile[210-215]:



These examples show the great importance of secondary steric effects for the type of reaction being investigated[216]. Actually, if the electron-acceptor substituents, which delocalise the negative charge mainly by a conjugation effect, cannot occupy a planar position in the transitional complex owing to interference with the sides of other groups, then the stabilisation of the anionic centre of such substituents is much worse, which can also lead to orientation of the attack of the nucleophile opposite to what is expected. Naturally, secondary spatial effects do not play a large part for groups which stabilise the anionic centre mainly by an induction effect (such as $CHal_3$, SO_2R, etc.). Probably for these very reasons bicyclo[2,2,2]octane-2,6-dione (XXII) is devoid of acidic properties[217], although it is a 1,3-diketone, whereas the trisulphone (XXIII) exhibits high acidity[218]:



It is noteworthy that the addition of the bulky anion of malonic ester to the carbon atom of cyanomethylenemalonic ester (XXI), which is already carrying two carboxyl groups[209], shows that primary steric effects play such a small part in this type of reaction[216]. The minor part played by these effects is also demonstrated by the example already given of the addition of amines to esters of β-trifluoromethylacrylic (V), β-trifluoromethylcrotonic (VI), and ββ-bis-(trifluoromethyl)acrylic (VII) acids. Whereas introduction of a CH_3 group into the β position of the first of the esters mentioned has no effect on the orientation in the addition, replacement of the methyl group by CF_3 in the second leads to a change in the direction of nucleophilic attack. Hence the orientation of nucleophilic addition is mainly due to electronic influences, not steric.

It was stated earlier that the approach to the problem of the orientation of nucleophilic attack from the position of a determination of the stability of carbanions from the dissociation constants of the corresponding substituted methanes is a crude simplification in many respects. Thus, in clear contradiction to this there is the example of the reactions of aryl β-nitrovinyl ketones. Although a comparison of $K_{CH_3NO_2} = 6.1 \times 10^{-11}$ and $K_{C_6H_5COCH_3} = 10^{-19}$ suggests that the direction of attack of nucleophilic reagents can be represented as follows:

$$RCOCH{=}CHNO_2 + HZ \rightarrow \underset{\displaystyle Z}{RCOCHCH_2NO_2},$$

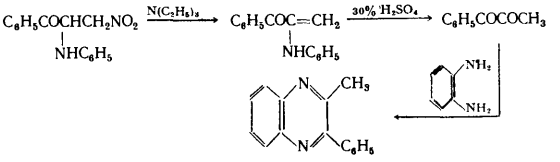
in reality, in addition to the products of the expected direction, products of the reverse orientation (and sometimes solely of the reverse orientation) are formed; it can be noted that for methanol[33,78] and aniline[219] both products belong to the kinetically controllable type.

Our own studies have repeatedly shown enhanced electrophilic nature of the ethylenic bond in these compounds. It was established that the reaction of aryl β-nitrovinyl ketones with aniline is exothermic[219]. As a result a mixture of the aryl α-anilino-β-nitroethyl ketone and the β-anilinovinyl aryl ketone is formed and the ratio of the products in the mixture depends on the nature of the substituent in the benzene ring:

$$ArCOCH{=}CHNO_2 + NH_2C_6H_5 \rightarrow \underset{\displaystyle NHC_6H_5}{ArCOCHCH_2NO_2} + ArCOCH{=}CHNHC_6H_5.$$

As Table 4 shows, the introduction of electronegative substituents (*p*-NO_2, *p*-Br) facilitates attack by the nucleophilic reagent at the β-carbon atom, and of electron donor ones (*p*-CH_3) at the α position.

Unfortunately, the dissociation constants of acetophenones substituted in the nucleus have not been determined. However, it is known that their enolisation, which is catalytically based, varies in the order H < *p*-Hal < *p*-NO_2.[220] The products liberated are kinetically controllable and cannot be interconverted. Thus under the action of bases α-anilino-β-nitroethyl phenyl ketone loses nitric acid, as a result of which α-anilinovinyl phenyl ketone is formed, the structure of which is shown by hydrolysis to methyl phenyl diketone:



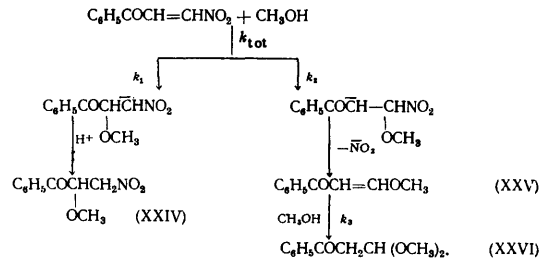
The dual direction of attack of the nucleophile was also observed by the example of the reaction of *trans*-phenyl

TABLE 4. Proportions of the products of the reaction of aryl 2-nitrovinyl ketones with aniline.

Ar	Proportions of the products of the reaction, mole %	
	aryl 1-anilino-2-nitroethyl ketone	aryl 2-anilinovinyl ketone
p-$CH_3C_6H_4$	> 95	< 5
C_6H_5	92	8
p-BrC_6H_4	60	40
p-$NO_2C_6H_4$	0	100

‡ Even if in this reaction chlorine atoms are first replaced by malonic ester residues, then this would have little effect on the capability of the $-CCl[CH(CO_2R)_2]_2$ group to stabilise the neighbouring anionic centre in comparison with the CCl_3 group.

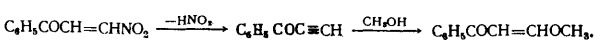
β-nitrovinyl ketone with methanol[78]. The reaction can be represented as follows:



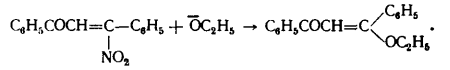
It takes place very readily and does not require a basic catalyst. Kinetic studies[33] showed that the reaction is pseudounimolecular in *trans*-phenyl β-nitrovinyl ketone and its overall rate (k_{tot}) considerably exceeds the rate of addition of methanol to other αβ-disubstituted ethylenes (see Table 5). It appeared that the reaction of β-nitrovinyl phenyl ketone proceeds irreversibly in both directions.

Moreover, it was found that the rate of formation of α-methoxy-β-nitroethyl phenyl ketone (XXIV) (α orientation), ($k_1 = 2.05 \times 10^{-3}$ min^{-1}) is only twice the rate of formation of β-methoxyvinyl phenyl ketone (XXV) (β orientation), ($k_2 = 0.92 \times 10^{-3}$ min^{-1}). Conversion of (XXV) into benzoylacetaldehyde dimethylacetal (XXVI) took place much more slowly ($k_3 = 9.1 \times 10^{-5}$ min^{-1}).

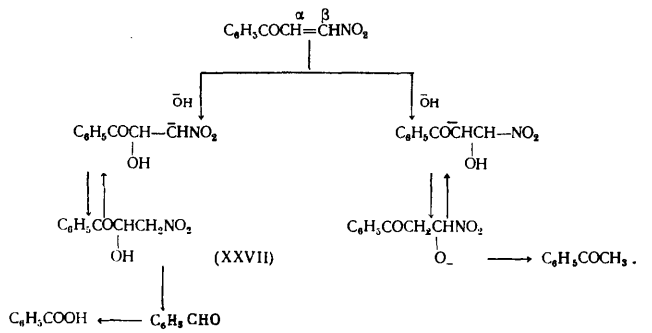
It was shown that the formation of β-methoxyvinyl phenyl ketone (XXV) is not connected with the elimination–addition mechanism which presupposes the intermediate formation of ethynyl phenyl ketone, since the ultraviolet absorption of the latter in standard buffer solution did not change in 24 h. After this period β-nitrovinyl phenyl ketone is almost completely converted into (XXIV) and (XXVI), and consequently the mechanism shown below does not take place:



The alternative mechanism of α elimination (HNO_2) with subsequent reaction of the carbene formed with methanol also seems improbable, since Smith and Davis[221] have shown that β-nitrobenzalacetophenone (which does not have an α-H close to the NO_2 group) reacts with the ethoxide ion to give β-ethoxybenzalacetophenone:



In the hydrolytic decomposition of β-nitrovinyl phenyl ketone the main products isolated were benzaldehyde and benzoic acid (products of α orientation of the OH^- ion), and there were traces of acetophenone (β orientation):[78]

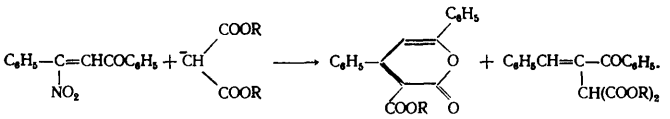


Here it is suggested that an intermediate α-hydroxy-ketone (XXVII) is formed, which on breaking down by a type of retrobenzoin decomposition[222-224], is capable of giving benzaldehyde.

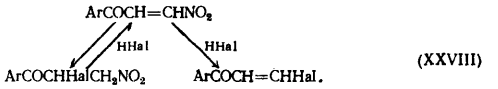
TABLE 5. Data on the kinetics of reactions with methanol of *trans*-αβ-disubstituted alkenes in standard buffer solution (0.0024 M CH_3CO_2H–0.0024 M CH_3CO_2Na) at 25°.

Alkene	k, min^{-1}	Ref.
$C_6H_5COCH=CHNO_2$	2.98×10^{-3}	33
$C_6H_5COCH=CHCOC_6H_5$	2.0×10^{-5}	18
$C_6H_5COCH=CHCN$	1.8×10^{-5}	17

A dual direction of attack by a nucleophile was also observed by Smith and Davis[221] in the example of the reaction of β-nitrobenzalacetophenone with sodiomalonic ester:



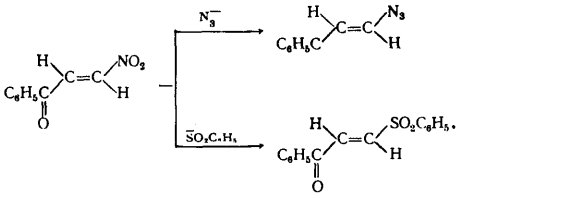
Aryl β-nitrovinyl ketones add on hydrogen chloride and bromide to form mainly aryl α-halo-β-nitroethyl ketones (XXVIII):[225]



Among the products of the reaction of β-nitrovinyl phenyl ketone with hydrogen chloride, *trans*-β-chlorovinyl phenyl ketone was observed. The formation of these products confirms the possibility of dual orientation of the attacking reagent.

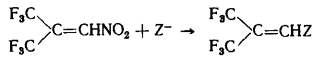
Note that when these hydrogen halides are passed for a long time into a solution of aryl β-nitrovinyl ketones the reaction is complex and leads to the formation of isoxazoles.

However, when *trans*-β-nitrovinyl phenyl ketone reacts with sodium azide or sodium benzenesulphinate[226] in aqueous alcoholic medium only products of replacement of the nitro-group which retain the *trans*-configuration are formed:



Hence the above examples of the reaction of the aryl β-nitrovinyl ketones contradict the orientation rule. Evidently these contradictions are due to several factors, which are not taken into account in the simplified approach to the orientation problem. Of such factors mention must first be made of the mutual influence of the groups entering the carbanion. The fact that these groups have an important influence is to some extent confirmed by the rather great sensitivity of the results of the reactions to the nature of the attacking nucleophile (compare the reactions with CH_3OH and $NH_2C_6H_5$ with those with N_3^- and $\overline{SO_2C_6H_5}$). The explanation of these anomalies is best provided by the hypothesis of the intermediate formation of π-complexes, the rearrangement of which into carbanions

is influenced by the nature of the groups entering into the carbanions. A noteworthy point is that the orientation rule is invalid for nitro-compounds in which the nitro-groups are replaced. It should be noted that, as already demonstrated[227], an anomalous course of reaction is also observed for $\beta\beta$-bis(trifluoromethyl)nitroethylene; $K_{CH_3NO_2} = 10^{-11}$, $K_{(CF_3)_2CFH} = 10^{-20}$: [39,40]



The nitro-group is known to be very easy to remove in nucleophilic substitution. Possibly its removal starts even before the π-complex is completely rearranged into the carbanion.

Furthermore, the influence of solvation can be of some significance and should be especially great for a solvent which strongly solvates anions (protonic solvents). The role of the solvent appears particularly clearly in the ionisation of $\geq$C–H acids activated by electron-acceptor groups. For example, nitromethane in aqueous medium with OH^- ions reacts 10^6 times more slowly than phenol, but in dimethylformamide proton transfer for both these acids is diffusion-controlled[228].

The decrease in the rate of ionisation of $\geq$C–H acids in proton-containing solvents is connected with the reconstruction of the solvate sheath, due to a change in the electronic structure on going from a neutral molecule to a mesomeric anion, unlike –OH or $>$N–H acids where there is no significant rearrangement of the electronic structure[228].

If it is assumed that this hypothesis is correct for the formation of anions by the ionisation of $\geq$C–H acids, then evidently it can be taken that solvation can also have considerable influence in the formation of carbanions by the addition of a nucleophilic reagent to a carbon–carbon double bond.

Naturally in $\alpha\beta$-disubstituted ethylenes different electron-acceptor groupings at the two ends of the ethylenic bond will be solvated differently. It can therefore be expected that the rate of formation of carbanions from these ethylenes will also show the influence of effects due to the rearrangement of the solvate sheaths. The difference in these effects can lead to some levelling of the rates of formation of the carbanions, in both the α and the β directions. Possibly such influence of the solvent will show particularly strongly in the reactions of substituted nitroethylenes.

In conclusion we must note that the problem of the orientation of nucleophilic attack at the double bond in XCH=CHY systems is too complex for it to be fully covered in the present review. Moreover, unfortunately this problem has not been studied systematically and with a purposeful direction. For this reason the present review only attempts to consider certain aspects of the problem.

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ETHYNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

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I. INTRODUCTION

Many papers have been published on the synthesis and study of the properties of unsaturated organoelemental compounds of the elements of Group IV of the Mendeleev Periodic System. Practical interest in these compounds arose in connection with the need to create new types of polymers. The investigation of the structure and reactivity of such compounds is of great theoretical importance since there is a specific interaction between carbon–carbon multiple bonds and the elements, an interaction which brings about the appearance of anomalous properties.

There is special interest in the unsaturated derivatives of the elements of the carbon subgroup since it is in this very series, situated at the heart of the Periodic System, that we can expect both an analogy with the purely carbon compounds, and also a considerable difference connected with the electronic structure of the atoms of the Group IV elements. Vinyl and allyl derivatives of silicon, germanium, tin, and lead have been studied most fully. The absence of reliable methods for the preparation of the ethynyl derivatives until recently retarded investigation in this field. It was only in the nineteen-forties, with the development of the chemistry of acetylene, that the first information appeared on the synthesis of alkynylsilanes[1,2]; the more systematic investigation of the alkynylsilanes started much later[3].

The first communication on the preparation of organogermanium compounds containing an acetylenic bond was published in 1958.[4] The first organotin acetylene derivatives were obtained in 1954.[5] A large number of acetylene derivatives of silicon, germanium, and tin are now known.

The present review considers only the acetylene derivatives of silicon, germanium, tin, and lead having a triple bond in the α or β positions to the atom of the element. Organoelemental compounds with a triple bond in the α position show most markedly the mutual influence of the π-electrons of the triple bond and the electrons of the element atoms.

The prop-2-ynyl derivatives of the Group IVb elements (C≡C in the β position) are interesting because they allow the influence of the elements on the prop-1,2-dienyl–prop-2-ynyl isomerism to be studied. The prop-1,2-dienyl derivatives formed as a result of the isomerisation are electronic analogues of ethynyl compounds (sp-hybridisation) [sic (Ed. of Translation)]; the resulting intramolecular interaction with the atoms of the Group IV elements should give effects analogous to those found with ethynyl groups [sic (Ed. of Translation)]. Therefore the preparation and properties of prop-2-ynyl compounds will also be considered within the bounds of our review.

This review describes in succession the synthesis and the chemical and physical properties of the ethynyl and

prop-2-ynyl derivatives of silicon, germanium, tin, and lead from literature sources, including work up to the middle of 1966.

II. PREPARATION OF ETHYNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

1. Preparation of Ethynyl Derivatives from the Alkali Metal Acetylides

This method allows compounds containing a triple bond in the α position to the element to be obtained:

$$(a)\quad R_{4-n}EX_n + MC{\equiv}CR' \rightarrow R_{4-n}E(C{\equiv}CR')_n,$$

where $n = 1, 2, 3,$ and 4; R = alkyl, aryl, H; X = Cl, Br; M = Na, Li.

$$(b)\quad 2R_3EX + MC{\equiv}CM \rightarrow R_3E{-}C{\equiv}C{-}ER_3.$$

Judging from the literature the method has certain limitations. Thus, with sodium acetylide in liquid ammonia alkynylsilanes and alkynylgermanes are not formed, evidently owing to ammonolysis of the alkyl- or aryl-silicon (or germanium) halides[10]. On the other hand all the organotin and organolead halogen derivatives react rapidly with NaC≡CR under these conditions[5-10] with the formation of disubstituted acetylenes ($R_3E{-}C{\equiv}C{-}ER_3$).

Quan and Cadiot[11] made a detailed investigation of the reaction of alkali metal acetylides with Ph_3SnX. They found that when triphenyltin iodide was used in this reaction and this was carried out rapidly, monosubstituted ethynyltriphenyltin(IV) was obtained.

The reaction of sodium acetylide with silicon and germanium halides was effected under other conditions. Thus in a patent[12] Boldebuch described the condensation of sodium acetylide with chloro(ethoxy)silanes in pyridine, with the formation of $(C_2H_5O)_{4-n}Si(C{\equiv}CH)_n$.

Beerman and Hartmann[5] obtained compounds of the type of $Ph_3E{-}C{\equiv}C{-}EPh_3$ by the reaction of monosodium acetylide with bromotriphenylsilane or triphenyltin bromide at 200°C. An analogous compound was obtained with lithium acetylide (through PhLi) in tetrahydrofuran[13].

Symmetrical organogermanium compounds with an acetylene bridge were obtained[14] by the reaction of sodium acetylide with chlorotriphenyl-and chlorotriethyl-germanium in tetrahydrofuran.

Davidson and Henry[15] prepared tetraethynylsilane, tetraethynylgermanium, diethynyldiphenylsilane, diethynyldiphenylgermanium, di-n-butyldiethynylgermanium, and ethynyltriphenylgermanium by the reaction of the corresponding germanium and silicon chlorides with sodium acetylides in tetrahydrofuran.

A patent[16] describes the preparation of ethynyl derivatives of tin, $R_{4-n}Sn(C{\equiv}CH)_n$, by the reaction of tin chlorides with alkali metal acetylides in ether, hexane, or benzene.

West and Kraihanzel[17] proposed a similar method for preparing

$$(CH_3)_3Sn(C{\equiv}CH).$$

Reaction with alkali metal acetylides has also been used for the preparation of poly-yne derivatives of tin and lead[11,18,19]. When the reaction is carried out in ether or hydrocarbons, then only the monosubstituted compounds are formed[17,18]. When the reaction is carried out in liquid ammonia the yield of mono- and di-substituted compounds depends on the ratio of the initial substances[11].

Some authors[20-27] have used the reaction of sodium and lithium acetylides of monosubstituted acetylenes with halogen derivatives of silicon, germanium, and tin for the preparation of compounds of the type $R_{4-n}E(C{\equiv}CR')_n$ and $R_3E(C{\equiv}C)_2R'$, where R = alkyl, aryl; and E = Si, Ge, or Sn.

For the preparation of $Pb(C{\equiv}CR)_4$ through the corresponding lithium acetylide rubidium hexachloroplumbate(IV) was used as the initial organolead compound[20] [sic (Ed. of Translation)].

2. Preparation of Ethynyl Compounds of Silicon, Germanium, Tin, and Lead Through Magnesium Bromide Derivatives of Acetylenes

$$R_{4-n}EX_n + XMgC{\equiv}CR' \rightarrow R_{4-n}E(C{\equiv}CR')_n,$$
$$R_3EX + XMgC{\equiv}C{-}R'{-}C{\equiv}CMgX \rightarrow R_3E{-}C{\equiv}C{-}R'{-}C{\equiv}C{-}ER_3.$$

Vol'nov and Reutt[1] first obtained alkynylsilanes by organomagnesium synthesis; as a result of the reaction of tetraethoxysilane with phenylethynylmagnesium bromide they obtained triethoxy(phenylethynyl)silane and diethoxybis(phenylethynyl)silane, and by reaction of ethynylmagnesium bromide with silicon tetrachloride, hexaethynyldisiloxane. At that time the use of polar solvents for the preparation of ethynylmagnesium bromide was unknown and the reaction was effected in boiling xylene; consequently, the yields of the products were insignificant.

After Jones[28] had developed the method of making ethynylmagnesium bromide in tetrahydrofuran, many investigators used this reagent for the preparation of ethynyl derivatives of silicon, germanium, and tin. Petrov and coworkers[23,29,30] synthesised alkynylsilanes of the type $R_3SiC{\equiv}CH$ and $R_2Si(C{\equiv}CH)_2$ from ethynylmagnesium bromide in tetrahydrofuran. Sladkov and Luneva[31] obtained diethynylmethylphenylsilane, diethynyldiphenylsilane, ethyldiethynylphenylgermanium, diethynyldiphenylgermanium, and *p*-bis(ethynyldimethylsilyl)benzene by the reaction of the corresponding germanium and silicon chlorides with ethynylmagnesium bromide in tetrahydrofuran. This method was also used to prepare monoethynyl derivatives of germanium[32] ($R_3GeC{\equiv}CH$) and tin[11,14]; to obtain the tin derivatives a method of precipitating the products from the reaction medium was used.

Mazerolles and coworkers[33] obtained tetraethynylgermanium by the reaction of germanium tetrachloride with ethynylmagnesium bromide.

Organomagnesium derivatives of monosubstituted acetylenes were used to make organoelemental ethynyl derivatives of the $R_{4-n}E(C{\equiv}CR')_n$ type[26,32-41], where E = Si, Ge, Sn; R = alkyl, aryl, vinyl.

Petrov and Shchukovskaya[3] found that symmetrical Iotsich reagent reacts with chlorotrialkylsilanes to form the corresponding symmetrical acetylene derivatives of silicon $R_3Si{-}C{\equiv}C{-}SiR_3$. At the same time Frisch and Young[42] condensed ethynylenedimagnesium dibromide with dichlorodimethylsilane in the presence of CuCl and as a result isolated

$$Cl(CH_3)_2Si{-}C{\equiv}C{-}Si(CH_3)_2Cl.$$

This reaction was used by many investigators[5,6,11,16,40] to prepare $R_3E-C\equiv C-ER_3$, where R = alkyl, aryl; E = Si, Ge, Sn.

Shikhiev and coworkers[43] carried out a similar reaction with butadiynylenedimagnesium dibromide:

$$BrMg-C\equiv C-C\equiv CMgBr + 2\,R_3SiCl \rightarrow R_3Si(C\equiv C)_2SiR_3.$$

Recently Shostakovskii and coworkers[44-46] reported the preparation of organotin acetylene compounds by the reaction of stannanols [hydroxo(trialkyl)tin(IV) complexes (Ed. of Translation)] and dialkyltin oxides [oxodialkyltin(IV) complexes (Ed. of Translation)] with an excess of magnesium bromide derivatives of monosubstituted acetylenes:

$$R_3SnOH + BrMgC\equiv CR' \rightarrow R_3Sn-C\equiv CR',$$

where R′ = vinyl, alkyl, aryl.

$$(R_2SnO)_n + 2n\,BrMgC\equiv CR' \rightarrow n\,R_2Sn(C\equiv CR')_2.$$

Alkynyl silanols are formed in the reaction of poly(diorganosiloxanes) with derivatives of ethynylmagnesium bromide[47-49]:

$$(R'R''SiO)_n + BrMgC\equiv CR \rightarrow R'R''(R-C\equiv C)SiOH.$$

3. Other Methods of Obtaining Ethynyl Organoelemental Compounds

a. Preparation through alkali metal derivatives of a triaryl- or trialkyl-tin. This preparation is based on the reaction of the sodium derivatives of tin with halogen derivatives of acetylene in liquid ammonia. Nothing has been published on the preparation of acetylene derivatives of silicon and germanium by this method and evidently this method is inapplicable for these compounds because the initial products may react with ammonia.

The reaction of sodium triphenylstannate(IV) or a sodium trialkylstannate(IV) with di-iodoacetylene produces the compound[5,10]: $R_3Sn-C\equiv C-SnR_3$.

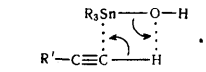
Compounds of similar structure can be obtained by the reaction of sodium triarylstannates(IV) or trialkylstannates(IV) with iodo- or bromo-acetylene[50]; in the first stage the sodium derivative of tin reacts with the labile hydrogen at the acetylenic carbon with the formation of $R_3SnC\equiv CBr$, which subsequently reacts again with the sodium derivative to form a disubstituted acetylene:

$$R_3SnNa + BrC\equiv CH \rightarrow R_3SnC\equiv CBr \xrightarrow{R_3SnNa} R_3SnC\equiv CSnR_3.$$

Reactions with halides of monosubstituted alkynes proceed analogously, with formation of $R_3Sn-C\equiv CR$.[19,51,52] $R_3Pb(C\equiv CR)$ were obtained in the same way[52].

b. Reaction of organic oxygen and amino-derivatives of tin with acetylene. Investigations showed that hydroxotrialkyltin(IV) complexes react with acetylene compounds containing labile hydrogen at the carbon with the triple bond, to form ethynyl derivatives of tin[53-57]. As a result of the reaction, trialkylstannyl derivatives of acetylene, vinylacetylene, and alkyl- and aryl-substituted acetylenes were obtained. The reaction with acetylene requires the use of pressure (15-20 atg) and elevated temperature (100-120°C)[57]. With vinylacetylene and phenylacetylene the reactions take place at room temperature and ordinary pressure[56,57]; this is explained by the increase in acidity of the acetylenic hydrogen.

The mechanism of the reaction is explained by the donor-acceptor interaction of the unpaired electrons of oxygen of the hydroxyl group with the labile acetylenic hydrogen and by the $d\pi$-interaction between the tin atom and the triple bond[56,57]:



The use of trialkyltin halides in this reaction seemed possible[58]. The method consists in the successive reaction of the tin compound with powdered alkali (NaOH or KOH) and the acetylenic compound:

$$R_3SnX \xrightarrow{NaOH} [R_3SnOH] \xrightarrow{HC\equiv CR'} R_3SnC\equiv CR'.$$

A new method was developed[53,55,59] for the preparation of acetylenic derivatives of tin, consisting in the direct reaction of monosubstituted acetylenes with bis(trialkyltin) oxides:

$$(R_3Sn)_2O + 2\,HC\equiv CR' \rightarrow 2\,R_3SnC\equiv CR'.$$

The reaction mechanism is evidently the same as for the stannols and proceeds in two stages:

$$R_3SnOSnR_3 + HC\equiv CR' \rightarrow R_3SnC\equiv CR' + R_3SnOH,$$
$$R_3SnOH + HC\equiv CR' \rightarrow R_3SnC\equiv CR' + H_2O.$$

Lutsenko and Ponamarev[60] described the preparation of trialkyl(phenylethynyl)tin complexes from trialkyl(methoxy)tin complexes and phenylacetylene. This reaction is more difficult than that with the hydroxotrialkyltin compounds and requires heating to 100-110°C.

Several other interesting preparations of acetylenic organotin compounds have been proposed.

Luijten and van der Kerk[61] observed the formation of organotin compounds in the thermal decarboxylation of triaryltin(IV) cyanoacetates:

$$(C_6H_5)_3SnOCOCH_2CN \xrightarrow{-CO_2} (C_6H_5)_3SnCH_2CN.$$

This method was next extended to the tin derivatives of phenylpropiolic and but-2-yndioic acids[61]:

$$R_3SnOCOC\equiv C-C_6H_5 \xrightarrow{-CO_2} R_3SnC\equiv CC_6H_5,$$
$$R_3SnOCO-C\equiv C-OCO-SnR_3 \xrightarrow{-2CO_2} R_3SnC\equiv CSnR_3.$$

In studying the reactions of nucleophilic substitution in organotin derivatives of dimethylamine it was found[62,63] that the N-Sn bond is readily split by compounds which contain a labile hydrogen, for example, phenylacetylene and hex-1-yne; acetylenic derivatives of tin are formed:

$$R_3Sn-N(CH_3)_2 + HC\equiv CR' \longrightarrow R_3Sn(C\equiv CR').$$

III. PREPARATION OF PROP-2-YNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

Le Quan and Cadiot[64] first reported the preparation of monoprop-2-ynyl derivatives of silicon and tin by the reaction of prop-2-ynylmagnesium bromide with trialkylhalogenosilanes and stannanes. This method became general for the preparation of most of the prop-2-ynyl derivatives of silicon, germanium, tin, and lead[18,31,40,65-67]:

$$R_{4-n}EX_n + BrMgCH_2-C\equiv CH \longrightarrow R_{4-n}E(CH_2-C\equiv CH)_n,$$

where n = 1, 2; R = alkyl, aryl; E = Si, Ge, Sn, Pb.

The reaction of lithium triphenylstannate with 1-bromoprop-2-yne was also used for the preparation of triphenylprop-2-ynyltin[67]. Note that here the prop-2-ynyl derivative is not formed, but exclusively its allene isomer with 30% yield. At the same time, chlorotriphenyltin and prop-2-ynylmagnesium bromide form only 10% of the allene isomer with a total yield of reaction products of 80%.[67]

IV. CHEMICAL PROPERTIES OF ETHYNYL ORGANOELEMENTAL COMPOUNDS

There has been little investigation of the chemical properties of the organoelemental compounds of acetylene described above. The reactions of these compounds, both nucleophilic and electrophilic, depend strongly on the nature of the element (Si, Ge, Sn, Pb) linked with ethynyl or prop-2-ynyl groups.

The reactions are considered below in the following order: (a) reactions with splitting of the E–C bond; (b) additions at the triple bond; (c) replacement of the acetylenic hydrogen; (d) isomerisation.

a. Reactions with splitting of the E–C bond. Many investigators have found that the Si–C≡ bond in alkynylsilanes is hydrolytically stable towards dilute acids and alkalis[5,40,68,69]. Concentrated solutions of alkalis break the silicon–carbon bond[5,68,69].

On changing alkyl groups at the silicon atom the higher homologues of the alkynylsilanes are less stable to the action of acids than the lower[68].

Bis(triphenylsilyl)acetylene is stable to cold water but is hydrolysed by alkalis[5]. Ethynyltriphenylsilane differs from the trialkylethynylsilanes in being hydrolysed in the cold[23].

The hydrolytic stability of the E–C≡ bond decreases in the order Si > Ge > Sn > Pb with increase in the polarity of the E–C≡ bond.

The disubstituted acetylenes $R_3E-C\equiv C-ER_3$, where R = aryl and E = Ge or Sn are fairly stable to atmospheric moisture but are split under the action of dilute alkali[10,16], unlike their silicon analogues. On replacing a phenyl radical by alkyls the sensitivity to moisture decreases[5,10]. Monophenylethynyl derivatives of germanium are fairly stable to atmospheric moisture but are hydrolysed by aqueous alkalis[21]. Strong organic acids[13] break the Ge–C≡ bond. Corresponding tin compounds are less stable and the hydrolytic stability decreases on replacing the triphenylstannyl radical by trialkylstannyl radicals[11,14]. Similarly, in trialkylstannylacetylene the Sn–C≡ bond is less stable than in triarylstannylacetylenes[11].

With increase in the number of acetylene radicals the sensitivity of the compound to hydrolysis increases[39]. All acetylene derivatives are extremely sensitive to water[5,9,20] and rapidly decompose in moist air. On the basis of a study of the hydrolytic splitting of the Sn–C≡ bond in triphenylstannylacetylenes it has been shown[11] that the ethynyl group is weakly bound to the tin atom and in the empirical series found by Seyferth[70] it should occupy a place before the aryl radical as regards ease of removal: ethynyl > aryl > vinyl > alkyl[11].

The increase in polarity of the E–C≡ bond in ethynyl organoelemental derivatives that results from the increase in the electronegativity of the carbon atom at the triple bond should therefore facilitate both electrophilic attack at the carbon atom and also nucleophilic attack at the atom of element E.

Copper and silver ions break the E–C≡ bond. Thus, $R_3Ge-C\equiv CH$ is split by silver nitrate in alcoholic solution and by an ammoniacal solution of CuCl, with the formation of silver and copper acetylides[32]:

$$R_3GeC\equiv CH \xrightarrow[NH_4OH]{Cu+} Cu-C\equiv C-Cu.$$

Under analogous conditions the ethynyl derivatives of tin and lead are decomposed with the formation of the same acetylides[5,9,11].

Breaking of Sn–C and Pb–C bonds is also observed under the action of Grignard reagents[5,11,45]:

$$R_3SnC\equiv C-R' + RMgBr \rightarrow R_4Sn + R'-C\equiv CMgBr.$$

The rate at which the C–E bond is broken by halogens also increases from Si to Pb. The Sn–C and Pb–C bonds in $R_3Sn-C\equiv CH$ and $R_3Pb-C\equiv CH$ are readily broken even under the action of iodine at room temperature with the formation of di-iodoacetylene and the corresponding organoelemental compound[5,11]. Even at room temperature bromine breaks the E–C bond in the ethynyl derivatives of germanium, tin, and lead[5,32,36,41].

In the organoelemental acetylene compounds containing a triple bond in the β-position to a silicon, germanium, tin, or lead atom the prop-2-ynyl radicals are much less strongly bound to the element atom than acetylene radicals would be. They are much less resistant to moisture, alkalis, acids[32,40,65]. Just like allyl and benzyl derivatives, the unsaturated radical in prop-2-ynyl compounds also exhibits electron-acceptor properties. Therefore the $E-CH_2$ bond breaks down and becomes more labile, which is explained by the σπ-conjugation of the 1–2 and 3–4 bonds associated with the electromeric effect.

b. Additions. Little has been published about additions at the triple bonds of ethynyl derivatives of the Group IVb elements. Compounds of the type $R_3EC\equiv CER_3$ and $R_3EC\equiv CR'$, where R' = H, alkyl, aryl, react differently with halogens. Alkynylsilanes do not react with iodine[5] and add only two atoms of bromine even on boiling in CCl_4.[30,35,39] It has been reported[71] that four bromine atoms add to $R_3Si-C\equiv C-CH_3$ but then HBr is lost and $R_3Si-CBr_2-CBr=CH_2$ is formed. At −80°C bromine adds to the triple bond of $R_3Ge-C\equiv CH$ but breaks the Ge–C bond in $R_3Ge-CH_2-C\equiv CH$.[32]

Davidson and Henry[15] brominated tetraethylgermanium with bromine at room temperature and isolated $Ge(CBr=CHBr)_4$ from the products.

Disilyl-substituted acetylenes do not add hydrogen under ordinary conditions for the catalytic hydrogenation of the C≡C bond; under severe hydrogenation conditions cracking of the molecule occurs[43,72,73].

$R_3Si(C\equiv CR')$ compounds are catalytically hydrogenated, two or four hydrogen atoms being added[39,43,72,73]. The monoethynyl derivatives of germanium $R_3GeC\equiv CH$, $R_3GeC\equiv CR'$, and $R_3GeCH_2-C\equiv CH$ readily add hydrogen at 20°C in the presence of Raney nickel, with the formation of saturated compounds[32,34].

Silicon and germanium hydrides are added quantitatively to alkynylsilanes and alkynylgermanes in the presence of hydrogen hexachloroplatinate(IV)[74,75]:

$$R_3Si-C\equiv CH + R_3Si-H \rightarrow R_3Si-CH=CH-SiR_3$$
$$R_3Ge-C\equiv CH + R_3Ge-H \rightarrow R_3Ge-CH=CH-GeR_3.$$

Diazomethane adds to diethynyldiphenylgermanium(IV) to form diphenyldipyrazolylgermanium(IV)[15].

Some recent papers describe investigations of the chemical reactions of enyne and diyne organoelemental compounds of silicon, germanium, and tin. Alkylvinylacetylenes are known to add bromine almost exclusively at the double bond[76]. Trialkyl(but-3-en-1-ynyl)silanes add bromine mainly in the 1 : 4 position:

$$R_3Si-C\equiv C-CH=CH_2 \xrightarrow[-10^\circ]{Br_2} R_3Si-CBr=C=CH-CH_2Br.$$

When heated, such dibromo-compounds isomerise to form the dibromo-1,3-diene.

Triphenyl(but-3-en-1-ynyl)silane exhibits low reactivity towards electrophilic reagents, as the triphenylsilyl group is a strongly electrophilic substituent and by drawing off electrons from the enyne system it makes the latter inactive towards bromination. Different substituents in the but-3-en-1-ynyl group at the double bond also effect the direction of bromination. Thus the introduction of a methyl group into but-3-en-1-ynyl(trimethyl)silane leads to a change in the direction of bromination, facilitating the addition of bromine at the double-bond[77-79]:

$$(CH_3)_3Si-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{Br_2} (CH_3)_3Si-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CBr}}-CH_2Br.$$

In vinyl- and allyl-dimethyl(but-3-en-1-ynyl)silanes bromination proceeds perferentially at the vinyl and allyl groups[79].

It has been shown that germanium-enynes also add bromine in the 1-4 and (partly) 3-4 positions[30,80]. When heated, the dibromides obtained are isomerised into dibromodienes. The direction of bromination in substituted germanium-enynes is less dependent on the substituent at the double bond than in the silicon-enynes, since the R_3Ge group compensates to a greater extent the influence of the alkyl groups at the double bond[77], because the R_3Ge radicals are less electrophilic than the R_3Si radicals. It is assumed[77-79] that the increase (in comparison with alkylvinylacetylenes) in the ability to add bromine in the 1, 4 position possessed by the silicon- and germanium-enynes is apparently due to an additional positive charge on the first carbon atom owing to electron displacement due to interaction of the *d*-orbitals of silicon and germanium with the π-electrons of the triple bond:

$$R_3E \longrightarrow C\equiv C-C=C.$$

Bromine breaks the Sn-C bond in tin-enynes[26,37]. The triple bond is more active in the catalytic hydrogenation of vinylacetylene hydrocarbons[81]. Trialkyl(but-3-en-1-ynyl)-silanes[78,79] ($R_3Si-C\equiv C-\underset{\displaystyle R'}{\underset{|}{C}}=CH_2$) add hydrogen preferentially at the double bond in the presence of $Pd/CaCO_3$ forming two addition products:

$$R_3Si-C\equiv C-\underset{\displaystyle R'}{\underset{|}{CH}}-CH_3 \text{ and } R_3Si-CH=C=\underset{\displaystyle R'}{\underset{|}{C}}-CH_3.$$

The ratio of the acetylene and allene isomers depends on the radical R′: the more bulky the radical the more allene isomer is formed[82].

Under these conditions germanium-enynes[74] are hydrogenated much more slowly than the corresponding silicon-enynes. The main direction of the reaction is the addition of hydrogen at the double bond but a certain amount of a diene derivative is formed. The existence of all three possible isomers has been found with the aid of infrared spectra[74]:

$$R_3Ge-C\equiv C-\underset{\displaystyle R}{\underset{|}{CH}}-CH_3$$

$$R_3Ge-CH=C=\underset{\displaystyle R}{\underset{|}{C}}-CH_3$$

$$R_3Ge-CH=CH-\underset{\displaystyle R}{\underset{|}{C}}=CH_2.$$

Under these conditions tin-enynes are not hydrogenated[79].

The difference in the direction of the catalytic hydrogenation of silicon and germanium-enynes of hydrocarbons is explained[74,82] by the steric factors under the conditions of heterogeneous catalysis (the presence of the bulky R_3E groups).

It is known[83,84] that alkylbut-3-en-1-ynes add alkyllithium complexes in the 1,4-position, with the formation of lithium derivatives of allene hydrocarbons. Under these conditions silicon-enynes and germanium-enynes form mixtures of isomeric allene and acetylene silicon hydrocarbons, the ratio of which depends on the structure of the enyne groupings and the nature of the radical in the alkyllithium[85-87].

Alkyl-lithium complexes break the Sn-C≡ bond in tin-enynes, with formation of tetra-alkyltin(IV) complexes[52,79,88].

From the above it is clear that nucleophilic (alkyl-lithium) and electrophilic (bromine, etc.) reagents break the Sn-C≡ bond. Zavgorodnii and Petrov[88] studied the stability of this bond in radical processes. It seemed that the triphenylmethyl radical adds to but-3-en-1-ynyltriethyltin(IV) mainly in the 3,4-position but to triethyl(3-methylbut-3-en-1-ynyl)tin(IV) in the 1,4-position, owing to steric factors[88] due to the presence of the methyl group. The same investigators also succeeded[88,90] in adding diazomethane to the above tin-enynes. The addition of diazomethane takes place at the double bond of the vinylacetylene residue, with formation of ethynylpyrazoline derivatives, from which cyclopropane compounds are subsequently formed:

$$(C_2H_5)_3Sn-C\equiv C-\underset{\displaystyle N}{\underset{\|}{C}}-\underset{\displaystyle NH}{\underset{\diagdown\diagup}{CH_2}} \rightarrow (C_2H_5)_3Sn-C\equiv C-\underset{\displaystyle CH_2}{\underset{\diagup\diagdown}{CH}}-CH_2+N_2.$$

Petrov and coworkers also investigated electrophilic and nucleophilic additions to trialkylsilylalkadiynes[91,92]. It was shown[93] that with 1,3-diene silicon-hydrocarbons the first molecule of bromine adds to the triple bond in the α-position to the silicon atom; when heated, the resulting dibromo-compound isomerises into 1,3- and 3,4-dibromo-compounds. This was shown by infrared and NMR spectra. An investigation of the addition of lithium alkyl-lithium complexes to 1,3-diyne silicon-hydrocarbons showed[92] that, irrespective of the nature of the radical in the LiR, the addition proceeds at the 3,4-position with fixation of the alkyl radical at the quaternary carbon atom. The results of the bromination and addition of LiR to silicon-diynes, carried out by the author, agree with the following scheme for the direction of polarisation of silicon-diynes, due to the $d\pi$-conjugation effect:

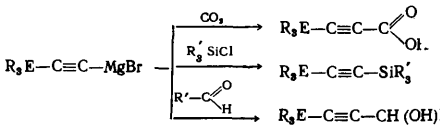
$$R_3Si-\overset{\delta-}{C}\equiv\overset{2}{C}-\overset{3}{C}\equiv\overset{\delta+}{\overset{4}{C}}-R.$$

c. Substitutions. The hydrogen atom at the H-C≡ bond retains its activity in silicon and germanium-substituted acetylenes. The ethynyl derivatives of silicon

and germanium readily form organomagnesium derivatives[23,30,32,94]:

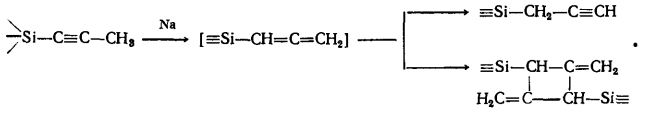
$$R_3E-C\equiv CH + R'MgX \rightarrow R_3E-C\equiv C-MgX + R'H.$$

These compounds can be used for the preparation of various germanium- and silicon-acetylene derivatives[30,32,95]:

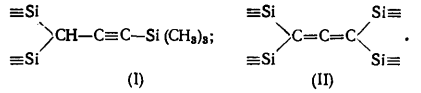


d. Isomerisation of acetylenic organoelemental compounds. Favorskii[96] investigated the isomerisation of acetylenic hydrocarbons; it has been discussed repeatedly[97,98].

There have been a few investigations[36,99,100] concerning the isomeric changes of acetylenic silicon hydrocarbons. Petrov and coworkers[36] obtained interesting results in an attempt to isomerise triethyl(prop-1-ynyl) silane into the allene isomer by the Favorskii reaction. Spectroscopic analysis of the products showed the presence of a cyclodimer and a little triethyl(prop-2-ynyl)silane:



West and coworkers[100] described the reaction of prop-1-ynyl-lithium with chlorotrimethylsilane, which led to the formation of a mixture of tri- and tetra-silyl derivatives:



(I) (II)

Thermolysis and photolysis of (I) leads to disproportionation and formation of an allene derivative.

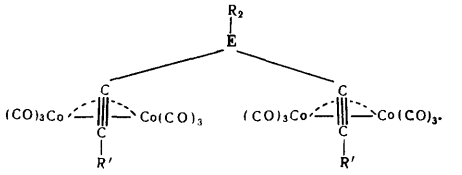
Investigators[20,31,38,40,62-64,101,102] who have been engaged in the preparation of prop-2-ynyl derivatives of organo-silicon, -germanium, -tin, and -lead compounds have noted that a mixture of allene, prop-2-ynyl, and prop-1-ynyl isomers is formed in the reaction:

$$R_3E-CH_2-C\equiv CH; \quad R_3E-CH=C=CH_2; \quad R_3EC\equiv C-CH_3$$

where E = Si, Ge, Sn, Pb; R = alkyl, phenyl.

The structure of the isomers obtained was studied by molecular and radio-frequency spectroscopy, and by analytical gas chromatography[20,63,101,102]. The amounts of the isomers obtained depend on the temperature, the basicity of the solvent, the order in which the initial compounds are added, and their structure[38]. With increase in the atomic weight of the element the proportion of allene isomers increases (Si < Ge < Sn < Pb)[63]. For example, in the preparation of triphenyl(prop-2-ynyl)-lead, 90% triphenyl(prop-1,2-dienyl)-lead(IV) is formed[20]. Prop-2-ynyl derivatives are especially readily isomerised into allene ones on heating in electron-donating solvents[67]. Thus when triphenylprop-2-ynyltin was boiled in 95% ethanol for 12 min it was completely converted into the allene isomer[67].

e. Other reactions. Hübel and Hoogzand[103] reported that trialkylethynylsilanes undergo cyclic trimerisation. Thus trimethylsilylacetylene forms 1,2,4-tris(trimethylsilyl)benzene at 100°C in the presence of tetracarbonylcobalt(IV)[103]. Possibly this reaction takes place through a stage of formation of an intermediate complex. This was confirmed recently by information published about the production of stable complexes from dialkynyl derivatives of silicon and germanium with tetracarbonylcobalt at room temperature in petroleum ether[104]:



V. PHYSICAL PROPERTIES

$R_3EC\equiv CR'$ and $R_3EC\equiv CER_3$, where E = Si, Ge, Sn, are liquids which can be distilled when R = alkyl and solids when R = aryl. The boiling point rises from the derivatives of silicon to those of tin. All the compounds are readily soluble in most organic solvents. Most of the liquid acetylene derivatives of silicon, germanium, and tin are thermally stable; they can be readily distilled. Solid acetylene derivatives of silicon and germanium usually melt without decomposition as distinct from the tin and lead derivatives, which usually melt with decomposition.

The dipole moments of the silicon- and tin-enynes were measured[105,106]. The tin-enynes have a greater dipole moment than hydrocarbons and silicon-hydrocarbons of analogous structure. The dipole moments are always directed from the tin or silicon towards the acetylene grouping[106]. Stadnichuk and Petrov[80] calculated the dipole moment of triethylvinylacetylenegermane [but-3-en-1-ynyltriethylgermanium(IV)], which had a greater dipole moment than the silicon-enyne of analogous structure[80].

Many papers on the spectra of ethynyl compounds of Group IVb elements have been published recently. Usually the infrared spectra of the compounds obtained are used to identify the structure. The most complete information on the vibrational spectra of ethynyl organoelemental derivatives is given in Chumaevskii's review[107] and in the papers of Petrov, Shostakovskii, and their coworkers[37,44], Cadiot[11,40], Hartmann[5,10], and others[108,109].

Of the special spectroscopic studies, that of Shigorin and coworkers[110] deserves mention.

The greatest interest is in the position and intensity of the characteristic frequencies of the C≡C and ≡C–H stretching vibrations.

Study of the infrared spectra of acetylene derivatives of silicon, germanium, tin, and lead showed the shift and change in intensity of the absorption bands characteristic of the acetylene bond[13,108,109,111-116]. For example, the stretching vibration of the acetylene bond in the t-butylacetylene spectrum corresponds to a frequency of 2110 cm^{-1}, that for ethynyltrimethylsilane 2040 cm^{-1}, and for triethylethynylsilane[112] the analogous vibration appears at $\nu_{C\equiv C}$ = 2008 cm^{-1}. The intensity of the absorption bands of the acetylenic bond in these compounds increases on going from carbon to tin[113,114].

It is known[115,116] that in unsymmetrical disubstituted alkynes the frequency of the stretching vibrations of the C≡C bond is in the 2200–2260 cm^{-1} region. Replacement of the carbon atom in the α position to the triple bond by a silicon atom[117] shows a drop in the frequency of the C≡C vibration of 75 cm^{-1}, and replacement of silicon by tin[115,116] leads to a further drop in frequency of 20 cm^{-1}.

Stadnichuk and Petrov investigated the infrared spectra of germanium-enynes[80] and showed that the triple bond in these compounds corresponds to an absorption band of 2147 cm^{-1}, that is, the same as in the silicon-enyne[116].

On the basis of the results obtained the authors conclude that the displacement of the triple bond vibrational band in the ethynyl derivatives of silicon, iron [germanium? (Ed. of Translation)], and tin is connected with a change in the bond polarity, which in turn can be explained by the intramolecular interaction of the π-electrons of the acetylenic bond with the vacant d-orbitals of silicon, germanium, and tin. By calculating the relative force constants of the triple bond in the acetylene derivatives of silicon and tin, the authors[116] were able to show that the displacement of the band of the triple bond of these compounds in the infrared spectra is not connected solely with the increase in mass of the atom on going from carbon to tin.

The peculiar light absorption of the α-ethynyl compounds of the Group IVb elements has also been associated with $d\pi$-conjugation[118,119].

To explain the shortening of the Si–O and Si–X interatomic distances in comparison with the sum of the covalent radii of the elements forming the bond, Pauling[120] postulated in the 1940's the possibility of the participation of the d-orbitals of silicon in the formation of bonds. Carbon has only s- and p-orbitals in its outer shells, whereas the other elements of Group IVb have the closer d-orbitals, which can in principle participate in the formation of a chemical bond. When the molecule of an organoelemental compound contains multiple bonds in the α position to the element, it is possible for intramolecular interaction to occur, with displacement of the π-electrons and use of the vacant d-orbital of the element. The possibility of the participation of the d-orbitals in the formation of chemical bonds was given a theoretical basis by Craig and coworkers[121], Eaborn[122], and others[123].

Stone and Seyferth[123] and Webster[124] also concluded that $d\pi$-conjugation is possible.

Husk and West[125] observed that in the ion-radical of dodecamethylcyclohexasilane the electron is delocalised over the entire molecule, which also confirms the participation of the d-orbitals of silicon in conjugation. The hypothesis of $d\pi$-conjugation has become widely accepted. At the same time, the problem of $d\pi$-conjugation forms the subject of discussion since as yet there is no method which would allow this effect to be evaluated directly and all the evidence in support of this phenomenon is based on indirect proofs.

From the vibrational spectra of vinyl derivatives of the Group IV elements, Leites and coworkers[126] concluded that the frequency of the C=C group in carbon and organotin compounds is connected solely with a change in the inductive effect of the element. Note also that Bochvar and Gambaryan[127] made quantum-mechanical calculations of the contribution of the d-orbitals of silicon and germanium to the bond formation in the vinyl compounds of these elements and found that it was very small and comparable in magnitude with the energy contribution of the p-orbitals of the carbon atom in compounds of analogous structure.

However, most research chemists still maintain the view that there is $d\pi$-conjugation between the vacant d-orbitals of the silicon, germanium, and tin atoms and the π-electrons of the unsaturated bonds situated in the α position to the hetero-atoms. There is still no single opinion as to the relative value of the $d\pi$-interaction in the derivatives of Si, Ge, Sn, and Pb. Some authors think that the $d\pi$-conjugation diminishes in the order Si > Ge > Sn[128], others, that is it independent of the element[129].

Gastilovich and coworkers[110] carried out an interesting investigation of the infrared spectra of the compounds

$$(CH_3)_3—CH_2—C\equiv CH \quad (I)$$
$$(CH_3)_3SiC\equiv CH \quad (II)$$
$$(C_2H_5)_3Sn(C\equiv CH) \quad (III)$$

in the region of the stretching vibrations of the C≡C and ≡C–H groups and calculated the effect of the mass of the element (from C to Sn), the rigidity of the E–C bond (E = Si, Sn), and of the intermolecular interaction on anomalies in the spectra and showed that these factors are insufficient to explain the displacement and change in intensity of the frequencies of the C≡C stretching vibrations, which is observed in compounds (II) and (III). On the basis of these results conclusions were drawn about the intramolecular interaction of the π-electrons of the triple bond with the d-orbitals of the Si and Sn atoms, which also determines the frequency change.

Another approach to evaluation of the $d\pi$-interaction in ethynyl derivatives of Si, Ge, Sn, and Pb from their infrared spectra has been made by Cadiot[11]. The author started from Kross's results[130] on the electronegativities of the Group IVb elements calculated from the frequencies of the infrared vibrations of the phenyl nuclei connected with the element and found a linear dependence of electronegativity on the C≡C bond frequency in $(C_6H_5)_3E(C\equiv CR)$. In appeared that the change in $\nu_{C\equiv C}$ in the order Si > Ge > Sn > Pb is connected with the decrease in electronegativity from Si to Pb which had been proposed by other authors[80,115], Cadiot[11] showed that on the basis of the Bykov equation[131], which relates the wave number of bands in the infrared spectrum with the electronic charge of the C≡C bond ($\nu^{2\alpha}_{C\equiv C} = KA_{C\equiv C}$), it can be concluded that the decrease in frequency for the C≡C bond in $\gtrless E-C\equiv C$ in the series from C to Pb is connected with the decrease in the charge on this bond; this is a consequence of the partial overlap of the π-electron cloud and the d-orbitals of the element.

The ultraviolet spectra of the ethynyl derivatives of silicon, germanium, and tin have also been investigated[11,18,108,109]. A bathochromic shift and increase in intensity of the bands has been observed in comparison with the acetylene hydrocarbons of analogous structure.

Comparatively recently there have been papers on the proton magnetic resonance spectra of the ethynyl compounds of the Group IVb elements[11,18,26,80,101,102,132,133]. For example, Egorochkin and coworkers[134] investigated the NMR spectra of ethynyltrimethylsilane and ethynyltrimethylgermanium(IV). The proton chemical shifts for the carbon atom of the ethynyl group are displaced to weaker fields compared with the proton shifts in saturated radicals, which the authors explain by the intramolecular interaction of the C≡C bond with the element atom. The large shift of the π-electrons towards the silicon atom compared with the germanium analogue leads to a more significant decrease in the electron density at the protons at the triple bond of the ethynylsilicon compounds. This is due to a stronger displacement of the chemical shift for ≡C–H to weaker fields in ethynyltrimethylsilane.

The NMR spectra of prop-2-ynyl compounds of silicon and tin have been obtained[101,102]; the chemical shifts of the protons of the methylene and acetylene groups decrease with decrease in the electronegativity of the elements and

are greatly dependent on the substituents at the elements, on the solvents, and on the concentration of the solution.

Simonnin[133] also investigated the NMR spectrum of compounds of the type $R_3E-(C\equiv C)_m-CH_3$ and $R_3E(C\equiv C)_m-H$, where E = Si, Ge, Sn and $m = 1, 2, 3$, labelled with ^{13}C in the α, β, and γ positions. The greatest difference in the chemical shifts of the ethynyl proton was observed in compounds with a $^{13}C-H$ bond (up to 39%).

Fedin and coworkers[132] found, in studying the NMR spectra of diethyldiphenyl-silane and -germane, that the silicon and germanium in these compounds are acceptors of electrons in relation to the phenyl nuclei. In diphenyldiprop-2-ynylgermane and diphenyldiprop-2-ynylsilane the signals of the ethynyl protons are shifted to stronger fields, by 0.8×10^{-6} for silicon and by 0.5×10^{-6} for germanium, relative to hexamethyldisiloxane.

Cadiot and coworkers[11,18] observed the proton chemical shifts in the NMR spectra of ethynyl compounds of tin. They interpreted the results from the standpoint of $d\pi$-conjugation.

To conclude this part of the review it must be emphasised that the hypothesis of $d\pi$-conjugation has been extremely fruitful and has stimulated considerably investigations in the field of the synthesis of ethynyl compounds of the Group IVb elements. This is equally true of the investigation of the physical properties of these compounds, particularly the infrared absorption spectra. Despite the fact that the interpretation of the spectral properties from the viewpoint of $d\pi$-interaction was evidently unsound, as a result of the work of many authors we have now, a large collection of spectral data, which is used successfully in chemical investigations for identification and for finding the structure of the compounds obtained.

VI. ORGANIC POLYMERS OF SILICON, GERMANIUM, AND TIN, CONTAINING ACETYLENIC GROUPINGS

The introduction of silicon, germanium, or tin into a polymeric chain is of great interest since, being situated in the same subgroup as carbon, they should have properties analogous to those of carbon, yet having a different electronic structure they should display their own specific properties.

Since the silicon, germanium, and tin atoms exhibit acceptor properties and their d-orbitals can draw away the π-electrons of a multiple bond, there is particular interest in polymers in which atoms of silicon, germanium, and tin alternate with acetylenic groupings. Such polymers could be expected to show interesting electrophysical properties. The first indication that such polymers could be made came in 1962 [135,136,137].

Korshak and coworkers[136] suggested that organosilicon and organogermanium polymers with acetylenic bonds in the chain could be synthesised by polycondensation of dihalogeno-organoelemental compounds with the bis-sodium (or bromomagnesium) derivatives of alkadiynes:

$$n\,R_2ECl_2 + n\,(Na)\,BrMg-C\equiv C-R'-C\equiv C-MgBr\,(Na) \longrightarrow$$
$$\longrightarrow [ER_2-C\equiv C-R'-C\equiv C]_n + 2n\,Mg\,Br\,(Na)\,Cl$$
$$n\,R_2ECl_2 + n\,BrMgC\equiv CMgBr \longrightarrow [ER_2-C\equiv C]_n,$$

where E = Si or Ge; R = CH_3, C_2H_5, or C_6H_5; R′ = $-C_6H_4-$.

Later a patent[138] described the preparation of polymers of the type

$$[ER_2-C\equiv C-R'-C\equiv C]_n$$

by the reaction of dilithium derivatives of alkadiynes with halogen compounds of silicon, germanium, and tin.

Sladkov and coworkers[139] proposed the preparation of organotin polymers with acetylenic groupings by the polycondensation of dialkyldimethoxystannanes and bisacetylenes:

$$n\,CH_3O-\underset{\displaystyle R}{\overset{\displaystyle R}{Sn}}-OCH_3 + n\,HC\equiv C-R'-C\equiv CH \longrightarrow \left[\underset{\displaystyle R}{\overset{\displaystyle R}{Sn}}-C\equiv C-R'-C\equiv C\right]_n;$$

where R = CH_3, C_4H_9; R′ = $-C_6H_4-$, $-GeR_2-$, or $-SiR_2-$

The authors confirmed[137,139] the structure of the polymers obtained from their infrared and NMR spectra. The polymers react with bromine only at elevated temperature (70–100°C), whereupon two bromine atoms are added at each triple bond[137]:

$$[ER_2-C\equiv C]_n \xrightarrow{n\,Br_2} [ER_2-CBr=CBr]_n.$$

$$[ER_2-C\equiv C-R'-C\equiv C]_n \xrightarrow{2n\,Br_2} [ER_2-CBr=CBr-R'-CBr=CBr]_n.$$

Hydrogenation of the polymers (20°C, Raney nickel) leads to the preparation of polymers with completely saturated bonds.

The organosilicon and organogermanium polymers which have been obtained are thermally stable up to 450–550°C; the organotin polymers, up to 300–350°C.[137]

Investigation of the electrophysical properties of the polymers has shown that organoelemental polymers in which atoms of silicon, germanium, and or tin alternate with unsaturated bonds exhibit high electrical resistivity at room temperature (10^{11}–10^{13} Ω cm) but it decreases with rise in temperature. The activation energy for conductivity by the polymers lies in the range 0.64–1.04 eV.[137]

A photo-e.m.f. (10 mV mW^{-1}) is observed with almost all the polymers that have been obtained[137,140].

It has been shown[137,141] that many of these polymers can be used as active electrographical layers.

A patent[138] has proposed the use of organoelemental polymers (where the element is silicon, germanium, tin, antimony, etc.) with acetylenic groupings for the manufacture of semiconductor materials.

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π-ALLYL COMPLEXES OF THE TRANSITION METALS

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I. INTRODUCTION

In the chemistry of organometallic compounds there is now great interest in the π-allyl complexes of transition metals. On the theoretical side this interest is explained by the unusual bond of the allyl ligand with the metal, which is an inherent feature of the bonds of both alkene and aromatic complexes (ferrocene, dibenzenechromium).

The results obtained in recent years show the considerable part played by π-allyl complexes as intermediates in various reactions of organic synthesis: they are extremely effective catalysts for stereospecific polymerisation and oligomerisation (both linear and cyclic) of alkenes and dienes.

In these complexes the bond between the transition metal and the allyl ligand, analogous to the π-cyclopentadienyl and arene complexes, is multicentric: all three carbon atoms of the allyl group take part in the formation of the bond with the metal owing to the more or less complete delocalisation of the double bond.

According to Fritz [1], the ligand in the π-allyl complexes can be a π-allyl anion, radical, or cation. According to the molecular orbital theory, with the [approx.] sp^2-hybridised carbon atoms of the allyl group there are one bonding, one non-bonding, and one antibonding orbitals [1,2]. Of the three electrons of the allyl radical, two are in a bonding orbital and one in an antibonding orbital. In the allyl anion, there is a pair of electrons in [each of] these orbitals, whereas in the cation the two electrons are located in the bonding orbital. Complex formation proceeds by the transfer of these π-electrons to a vacant orbital of the metal†.

Because atoms of metals which form π-allyl complexes have lone pairs of *d*-electrons the possibility arises for formation of dative bonds by the interaction of these electrons with the antibonding orbitals of the π-allyl anions. Quantum-mechanical calculations show that the participation of the π-allyl ligand in a dative bond is less significant, unlike an alkenic ligand [3]. This, in particular, can explain the low stability of the so-called "pure" allyl compounds of the transition metals, that is, those in which there are no other stabilising ligands. In the presence of ligands such as CO, Cl, or C_5H_5 the stability of the complexes increases, this being explained by the lower energetic level of the antibonding orbitals of these ligands (in comparison with π-allyl) which also capture the *d*-electrons of the metal, forming a dative bond.

The first π-allyl complex was apparently made in 1952 by Prichard [4] in the reaction between a hydrocarbonyl of cobalt [hydrogen tetracarbonylcobaltate(−1)] and butadiene. The author erroneously ascribed to this compound the structure of a 1:1 addition compound $C_4H_7Co(CO)_4$. Later, Jonassen and coworkers [5] found that the reaction of hydrogen tetracarbonylcobaltate(−1) with butadiene is accompanied by the release of one molecule of carbon monoxide and suggested that in the product $C_4H_7Co(CO)_3$ the bond of the 1-methylallyl ligand with the metal is effected by one π- and one σ-bond [6]. Such a conception of the nature of the bonding of the allyl residue to the transition metal was viewed with suspicion after both Syrkin and coworkers [7] and Smidt and Hafner [8] obtained chloro-(π-allyl)palladium(II) $(C_3H_5PdCl)_2$. Soon after Heck and Breslow [9] used nuclear magnetic resonance to show the π-allyl structure of the compound $C_3H_5Co(CO)_3$.

π-Allyl complexes have now been obtained for all the transition metals of Groups IV–VIII except Hf, Re, Tc, and Os.

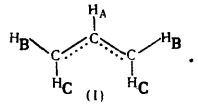
II. INVESTIGATION OF STRUCTURE

1. NUCLEAR MAGNETIC RESONANCE SPECTRA

The proton magnetic resonance method enabled slight differences in the structure of the allyl compounds of the transition metals to be observed. On the basis of their NMR spectra they can be classified into four types.

a. π-Allyl Compounds

The NMR spectra of the π-allyl complexes of cobalt [9,10], manganese [10], palladium [11,12], nickel [12], and some other metals are characterised by the presence of three types of signal with ratio of intensities 1:2:2 (Fig. 1*a*). The interpretation of the NMR spectra also leads to a structure for the complexes in which, owing to the delocalisation of the π-electrons, hybridisation of the allyl carbon atoms (which are in the same plane) occurs. The hydrogen atoms H_A, H_B, and H_C in (I) are evidently coplanar with the carbon atoms:



(I)

The different chemical shifts for the H_B and H_C hydrogens suggests that they are at different distances from the metal, with the H_C protons, which are closer to the metal atom, showing a shift at higher field intensities, owing to the greater screening by the metal atom. The proton at the central carbon atom, H_A, is further from the metal atom than the H_B and H_C protons and is therefore characterised by the least chemical shift. A similar conclusion can be drawn from a comparison of the spin–spin coupling constants J_{AC} and J_{AB}, the first of which is always the greater. The interaction between the protons H_B and H_C is almost zero, a possible explanation for this, according to Gutowsky and coworkers' results [13], being that the angle $H_C\!-\!C\!-\!H_B$ is close to 125°C. The introduction of a polar substituent (for example, a chlorine atom) at the central atom of the allyl group leads to the observation of some interaction between the protons H_B and H_C (J_{BC} = 2 Hz) [14]. On replacing the H_A hydrogen by alkyl groups simple spectra are also obtained: the signal with chemical shift 4.5–4.9, which belongs to the H_A proton, disappears, and a peak with chemical shift τ = 7.7–7.9, corresponding to the allyl group protons attached to the central carbon atom of the π-allyl group, is observed [15].

The spectra of π-allyl complexes substituted at a terminal carbon atom of the allyl group are more complex,

† However, the problem of how many electrons (2, 3, or 4) leave the π-allyl ligand to form the bond with the transition metal is not so important, since this, in turn, is compensated by the degree of oxidation of the central atom.

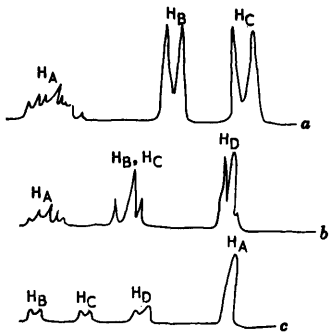
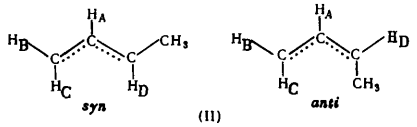


Fig. 1. NMR spectra of allyl compounds: *a*) π-allyl; *b*) σ-allyl; *c*) πσ-allyl.

the bands showing splitting due to the terminal alkyl group. For simplicity, we will discuss only 1-methyl-π-allyl (π-crotyl‡) complexes. The replacement of the H_B or H_C hydrogens of the π-allyl group leads to two isomeric complexes depending on the position of the methyl group in relation to the H_A hydrogen at the central atom of the π-allyl group—*syn*-(II) and *anti*-(II) respectively.



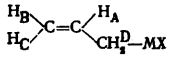
(II)

The spectra of $[(C_4H_7)Co(CO)_3]$ [10,16] and $(C_4H_7NiCl)_2$ [12] show five types of split peaks with the intensity ratio 1:1:1:3:1. The example of 1-methyl-π-allylcobalt-tricarbonyl showed that the spin–spin coupling constant J_{AD} is 10.5 Hz for the *syn*-isomer and 6.8 Hz for the *anti*-isomer [16]. Here the presence of the π-allyl structure is also confirmed by the equality of J_{AC} and J_{AB} for the *syn*-isomer and the similar values of J_{AB} and J_{AD} for the *anti*-isomer.

The possibility of *syn–anti*-isomerism is excluded for complexes with cyclic π-allyl ligands and therefore the NMR spectra of such compounds mainly contain three types of bands. Here it must be pointed out that the chemical shift for the H_A and H_B protons of (II) is quite close to the shift for the same protons of the unsubstituted π-allyl group of (I) [17]. The resonance lines of the methylene protons of a cyclic ligand appear at higher field strengths (τ = 8.5–9).

b. σ-Allyl Compounds

The σ-allyl compounds (III) are characteristic mainly of the non-transition elements. Of the transition metals, only Mn [10], Fe [18], W [19], and Mo [20] are known to form such compounds. In the NMR spectra of the compounds of this group four signals with the intensity ratio 1:1:1:2 are usually observed (Fig. 1*b*),



(III)

‡ sic (Ed. of Translation).

that is, the protons H_B and H_C are non-equivalent owing to the impossibility of rotation about the C=C bond. The signal from the H_A proton is split into a complex multiplet by the H_D and H_B nuclei, so that J_{CA} is considerably less than J_{AB}, as is usually observed for *cis–trans* hydrogen atoms in alkenes [21]. The signals from the H_B and H_C protons are split into a doublet by the H_A nucleus, but since these protons belong to the AC system both doublets overlap and three lines are usually obtained. Finally, the signal from the H_D protons is split into a doublet by the H_A nucleus.

c. "Dynamic" Allyl Compounds

The NMR spectra of compounds of this type show two signals with a 4:1 intensity ratio, that is, the CH_2 group protons have become equivalent. For the allyl compounds of non-transition metals (for example, magnesium [22]) this is explained by a rapid rearrangement of the type:

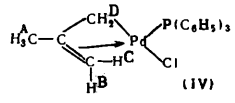
$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}MX \rightleftarrows XM-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH_2}.$$

An analogous NMR spectrum was obtained at elevated temperatures for addition compounds of π-allyl- (or π-methyl-allyl-)palladium chloride with triphenylphosphine [23-26], dimethyl sulphoxide [25-27], and triphenylarsine [26]; of π-allyl-nickel chloride with triphenylphosphine [23]; of π-allylnickel bromide and cyanide with triethylphosphine [28]; and also for allyl compounds of thorium and zirconium [23,27,29]; and for complexes $C_3H_4RRh(X_2)[P(C_6H_5)_3]_2$ and $C_3H_5Pt(X).[P(C_5H_5)_3]_2$, [30] where R = H, CH_3; X = Cl, Br.

The equivalence of the CH_2 groups in the complexes mentioned above can be explained as follows: as a result of the deficit in *d*-electrons necessary for the formation of dative bonds between the metal and the π-allyl ligand it becomes possible for the latter to rotate around the axis passing through the metal atom and the centre of the CCC plane. According to the results of Wilke and coworkers [23] the energy barrier of this rotation is 10–15 kcal.

d. πσ-Allyl Compounds

These intermediate structures were observed for the 1:1 addition compound of π-methylallylpalladium chloride with triphenylphosphine [24-25]. In the NMR spectrum of this compound (IV) there are four signals with intensity ratio 1:1:2:3 (Fig. 1*c*):



(IV)

The signals from the protons H^B, H^C, and H^D are split into doublets by the interaction with the phosphorus atom.

2. INFRARED AND ULTRAVIOLET SPECTRA

Fritz [1] made the first detailed study of the infrared spectra of a series of π-allyl complexes of palladium and nickel.

Weak bands at 3079, 3040, 3010, and 2907 cm^{-1} were assigned to stretching vibrations of the CH_2 (ν_{CH_2}) and CH (ν_{CH}) bonds. The stretching vibrations at lower wave

numbers are due to the C–H_C bonds (I) situated close to the metal atoms. For $(C_3H_5NiCl)_2$ and $(C_3H_5PdBr)_2$ these absorption bands were observed at lower frequencies (2865 and 2849 cm^{-1} respectively)[12].

The interpretation of bands belonging to the vibrations of the carbon skeleton of the π-allyl group is of the greatest value in determining the structure of the complexes. Lanpher[31] showed that the allyl anions have an absorption band in the 1500–1560 cm^{-1} region: in the π-allyl complexes of the transition metals coordination leads to a displacement of the C–C asymmetric stretching vibrations (ω_{CC}) into the 1450–1470 cm^{-1} region[1,12,32]. The bands at 1021 and 511 cm^{-1} were attributed to the symmetric stretching vibrations of the C–C bonds (ω_{CC}) and the deformation vibrations of the C–C–C carbon skeleton (Δ_{CCC}) of the allyl group respectively. The bands at 1450–1470, 1021, and 511 cm^{-1} are characteristic of π-allyl systems. For the π-crotyl and π-methylallyl complexes of palladium and nickel Δ_{CCC} appears in the 520–567 cm^{-1} region[1,12,33] and for the complexes with cyclic ligands[1] it is at ~ 585 cm^{-1}.

The absorption bands at 1381, 1226 and 1191 cm^{-1} are attributed to the in-plane bending [scissoring] vibrations of the CH_2 (δ_{CH_2}) and CH (δ_{CH}) bonds and those at 981, 965, 940, 911, and 763 cm^{-1} to the out-of-plane bending [wagging] vibrations of the CH_2 (γ_{CH_2}) and CH (γ_{CH}) bonds.

Lupin and coworkers[34] dealt with the interpretation of the vibrational frequencies of the Pd–Cl bond in bridging allyl complexes.

The comparative instability of π-allyl complexes towards ultraviolet radiation greatly limits the possibility of studying them by this method. The limited information on the ultraviolet spectra of certain π-allyl complexes, mainly those of nickel and palladium[35–37], has not yet been satisfactorily explained.

3. X-RAY STRUCTURAL INVESTIGATIONS

X-Ray structural investigations of π-allylpalladium chloride, carried out by several investigators[38–43] have confirmed the structure proposed on the basis of the NMR and infrared spectra, in which the double bond of the allyl group is completely delocalised and the group is bonded with the metal directly by a π-bond analogous to the bond between the cyclopentadienyl ring and a metal atom.

It is expedient to give only the results of the analysis of three-dimensional projections of the $(C_3H_5PdCl)_2$ molecule[39–41] since they are much more accurate than the results of Rowe[43] and Porai-Koshits[38], who studied two-dimensional projections of crystals of the complex. Fig. 2 shows the intramolecular distances and angles for bis-(π-allylpalladium chloride). It was shown that, in contrast to other results[38,43], the plane of the three carbon atoms of the allyl groups is not perpendicular to the plane of the bridging system, $(PdCl)_2$: the angle between these planes is 108°C, and the central carbon atom of an allyl group is 0.05 Å above and the terminal carbon atoms are 0.04 and 0.09 Å below the plane of the palladium atoms [sic: presumably palladium and chlorine atoms is meant]. The large angle between the C–C–C carbon atoms of the allyl group (128.6°C ± 3.3°C) agrees well with the fact that in $(C_3H_5PdCl)_2$ it behaves as a bidentate ligand.

An X-ray structural analysis made by Smith[42] at −140°C confirmed in the main Oberhansli and Dahl's results[39–41]. However, according to Smith's results the three carbon atoms

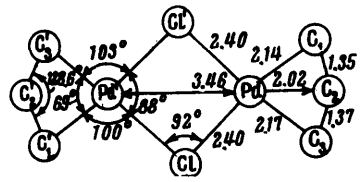


Fig.2. Intramolecular distances and angles in $(C_3H_5PdCl)_2$.

of the π-allyl group are at an equal distance from the palladium atom. The low-temperature investigation also established that all five hydrogen atoms lie in the same plane as the carbon atoms.

These have also been X-ray diffraction studies of bis-(π-methylallyl)nickel[44], cyclo-octenylnickel acetylacetonate[45], π-allylpalladium acetylacetonate[46], cyclo-octa-2,4-dienylpalladium acetylacetonate[47,48], the addition product of π-methylallylpalladium chloride and triphenylphosphine (VI)[49], π-allyl-π-cyclopentadienylpalladium[50], and π-allylirontricarbonyl iodide[51].

4. MEASUREMENT OF DIPOLE MOMENTS

The dipole moments found for π-allyl-π-cyclopentadienylnickel (0.78 D)[12,52] or π-cyclopentadienyl-π-cyclopentenylnickel (1.16 D)[53] agree well with the sandwich structure proposed for them. The appreciable dipole moment observed for dicarbonyl-π-cyclopentadienyl-π-cyclopentenylchromium (3.49 D)[54,55] indicates the asymmetric structure of the complex with the carbonyl groups in the *cis*-position.

The appearance of appreciable dipole moments in the π-allylhalogeno-complexes of nickel (1.3–1.6 D) and palladium (2.1–2.2 D) which are symmetrical in the crystalline state[7,8,12,52,56,57] suggests that evidently the centrosymmetrical configuration of these complexes undergoes considerable deformation in solution. Syrkin and coworkers[7] attributed the dipole moment of $(C_3H_5PdCl)_2$ in benzene to partial dissociation into the monomer, whereas Fischer and Bürger[12,52,57] suggested that the appearance of a dipole moment in these dimeric complexes can be explained by the angular displacement of the bridging halogen atoms. Moreover, during the dissolution of these compounds reorientation of the two allyl ligands from the *trans*-to the *cis*-position is possible (Fig. 3), which also can significantly affect the value of the dipole moment.

The first, and still the only, example of mirror [optical] isomerism in a transition metal π-allyl complex was described by Corradini and coworkers[58].

III. PREPARATION AND PROPERTIES

Owing to the great variety of both π-allyl complexes themselves and of methods for preparing them, it is desirable to examine the latter for each metal separately.

1. COMPLEXES OF TITANIUM, ZIRCONIUM, THORIUM, VANADIUM, NIOBIUM, AND TANTALUM

π-Allylbis-(π-cyclopentadienyl)titanium can be obtained by the reaction of bis-(π-cyclopentadienyl)titanium halides

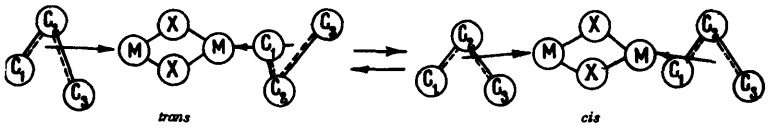


Fig.3. *cis–trans* Isomerism of halogeno-(π-allyl) complexes. M = Ni or Pd; X = Cl, Br, or I.

with allylmagnesium chloride in tetrahydrofuran solution[59,60]. The substance isolated by recrystallisation from *n*-pentane at −80°C consists of purple crystals, m.p. 118°C (decomp.). This complex and its pentane solutions are stable for a few months at room temperature in the absence of oxygen but in air rapid oxidation occurs. Reaction with octanol is accompanied by the liberation of propene in 80% yield: in methylene or allyl chlorides, $(C_5H_5)TiCl_2$ is formed. The compound is paramagnetic. The π-allyl structure has been advanced solely on the basis of infrared spectra. 1-Methyl- and 1,3-dimethyl-π-allyl-bis-(π-cyclopentadienyl)titanium have been prepared by the reaction of $(C_5H_5)_2TiCl_2$ with isopropylmagnesium bromide in the presence of buta-1,3-diene and penta-1,3-diene respectively[61].

The reaction of allylmagnesium chlorides with titanium, zirconium, thorium, vanadium, niobium, and tantalum salts [halides (Ed. of Translation)] gave the corresponding "pure" allyl compounds[23,29].

2. CHROMIUM COMPLEXES

Kurras and Klimsch[62] and Oberkirch[63] obtained tris-(π-allyl)chromium by the reaction of anhydrous $CrCl_3$ with allylmagnesium halides in ether at a temperature not exceeding −18°C. It forms red-black plates, which melt with decomposition at 77–79°C. According to cryoscopic measurements, the compound is monomeric. Solid tris-(π-allyl)chromium is extremely unstable and decomposes at −16°C, but the compound can be stored as a solid and in solutions for some time at −80°C. Bis-(π-allyl)chromium(III) was observed in the decomposition products: it is a dimer with a metal–metal bond[64]. The interaction of $(C_3H_5)_3Cr$ with hydrogen halides leads to the formation of bis-(π-allyl)chromium halides[63,65]. The latter can also be obtained as a result of the action of halogens on $(C_3H_5)_3Cr$, the course of the reaction depending considerably on the polarity of the solvent[63]. For example, $(C_3H_5)_3Cr$ and iodine in ether give bis-(π-allyl)chromium iodide, but when the reaction takes place in toluene the reaction leads only to chromium(II) halides.

When a mixture of $[(C_5H_5)Cr(CO)_3]_2$ and butadiene is irradiated with ultraviolet rays for 6 h in the presence of small amounts of mercury metal dicarbonyl-1-methyl-π-allyl-π-cyclopentadienyl is formed[66,67]. In this complex the 1-methyl-π-allyl ligand is in the *syn*-form but the CO groups are in the *cis*-position[35].

A compound similar in structure with a π-cyclopentadienyl ligand is obtained in low yield by the reaction of bis-(π-cyclopentadienyl)chromium, carbon monoxide, and hydrogen at 65–68°C.[54,55] The complex is stable in air and readily dissolves in polar organic solvents. Its NMR spectrum has four signals with intensity ratio 5:1:2:4, which agrees with the π-allyl structure of the complex. The presence in the infrared spectrum of two close absorption bands at 1894 and 1818 cm^{-1} shows the *cis*-position of the CO groups.

3. COMPLEXES OF MOLYBDENUM AND TUNGSTEN

When σ-allyl complexes of molybdenum and tungsten, which are obtained in high yields by the reaction of the sodium salt $Na^+[M(CO)_3(C_5H_5)]^-$ with an excess of allyl chloride, are subjected to ultraviolet irradiation in a vacuum, π-allyl complexes of these metals are formed[19,20]:

$$(\pi\text{-}C_5H_5)\,M\,(\sigma\text{-}C_3H_5)\,(CO)_3 \xrightarrow{uv} (\pi\text{-}C_5H_5)\,M\,(\pi\text{-}C_3H_5)\,(CO)_2 + CO.$$

Dicarbonyl-π-allyl-π-cyclopentadienylmolybdenum (or tungsten) differs from the initial complexes with π-allyl ligands in having considerably greater thermal stability and also great resistance to oxidation by oxygen.

According to King's results[68], in the complex $[(\pi\text{-}C_5H_5).(C_7H_7)Mo(CO)_2]$, obtained from $[(C_7H_7)Mo(CO)_2]I$ and cyclopentadienylsodium, the bonding of the molybdenum with the cycloheptatrienyl ligand has a π-allyl nature. The author came to this conclusion as a result of a comparison of the NMR spectra of this compound and of $[\pi\text{-}C_5H_5)(\sigma\text{-}C_5H_5)Fe(CO)_2]$[69].

King also succeeded in obtaining the complex $[(\pi\text{-}C_3H_5).(C_9H_7)Mo(CO)_2]$ from tricarbonylindenylmolybdenum and allyl chloride[70].

Murdoch[71] obtained new π-allyl complexes of molybdenum and tungsten, not containing π-cyclopentadienyl groups, in good yield from the tetraethylammonium salts of the halogenopentacarbonyl complexes of these metals and the allyl halides:

$$2\,[(C_2H_5)_4N]^+[MX(CO)_5]^- + 3\,R{-}C_3H_4Y \rightarrow [(C_2H_5)_4N]^+[M_2Y_3(R{-}C_3H_4)_3(CO)_4]^- + 6\,CO + R{-}C_3H_4X + [(C_2H_5)_4N]^+X^-,$$

where X = Cl, Br, or I; Y = Cl or Br; R = H or CH_3; and M = Mo or W.

These complexes are yellow crystalline substances, readily soluble in polar solvents. In air, the tungsten complexes are always less stable than the molybdenum.

The complex anions have a dimeric structure with halogen bridges between the metal atoms. Reaction of the molybdenum complexes with pyridine, 2,2′-bipyridyl, and ethylenediamine leads to the formation of monomeric complexes, for example, $R{-}C_3H_4Mo(CO)_2(C_5H_5N)_2Y$.[72] The latter work also describes the replacement of the halogen bridges Y by the groups OCH_3, OC_2H_5, SC_6H_5, and OH.

There are indications of the possibility of obtaining dimeric bis-(π-allyl)molybdenum and tetrakis-(π-allyl)-molybdenum and tungsten by the reaction of allylmagnesium chloride with molybdenum pentachloride and tungsten pentabromide[63,73,74].

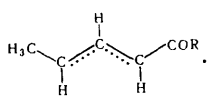
4. MANGANESE COMPLEXES

Two main methods for obtaining π-allyl complexes of manganese are known: (a) from the alkali salts of pentacarbonylmanganese and allyl halides[10,75,76]; (b) by the addition of $HMn(CO)_5$ to dienes[10].

In both instances complexes of the general formula allyl–$Mn(CO)_5$ are formed in the first stage of the reaction, these complexes containing σ-allyl ligands. On heating these compounds one molecule of carbon monoxide is lost and tetracarbonyl-π-allylmanganese complexes are formed. The infrared spectra show that the π-allyl complexes differ from the σ-allyl complexes in the presence of an absorption band at 1505 cm^{-1} and the absence of an intense absorption band at 1620 cm^{-1}, which is ascribed to the stretching vibrations of the non-coordinated double bond[10].

The above methods were used to prepare manganese π-allyltetracarbonyl complexes with the following ligands: allyl, 1-methylallyl, 2-methylallyl, 1-chloroallyl, and 1,1-dimethylallyl[10].

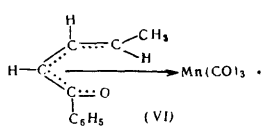
Recently Bannister and coworkers[77,78] reported another way of making π-allyl complexes of manganese. They found that phenyl-or methyl-pentacarbonylmanganese reacts readily with butadiene, forming a 1 : 1 addition product with the ligand of structure (V; R = CH_3, C_6H_5):



(V)

The mechanism of these processes was studied by Green and Hancock[79].

An interesting reaction took place on heating the complex with R = phenyl to the melting point (~ 108°C). Slow release of a molecule of carbon monoxide gave a new complex (VI) [from the allyl $Mn(CO)_4$ species (Ed. of Translation)] in which, according to the authors[80]§ the ligand was a five-electron system analogous to the three-electron system described below for tricarbonyl-π-oxapropenylcobalt.



(VI)

5. IRON COMPLEXES

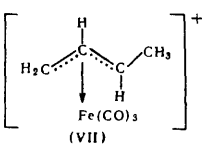
π-Allyl complexes or iron can be obtained in various ways, of which the two most general are: the action of strong acids on the π-(1,3)-dienecarbonyl complexes of iron, and the reaction of allyl halides with iron carbonyls—$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.

a. Action of Strong Acids on π-(1,3)-Dienecarbonyl Complexes of Iron

Impastato and Ihrman[81] found that tricarbonylbutadieneiron reacts at room temperature with anhydrous hydrogen chloride to give the 1 : 1 addition product of tricarbonylbutadieneiron and HCl in up to 45% yield. An investigation of the infrared spectra made by the authors showed that this compound is tricarbonyl-(1-methyl-π-allyl)iron chloride. The compound was also obtained by the reaction of tetracarbonylbutadieneiron with hydrogen chloride[82]. In the first stage of this reaction an intermediate cationic carbonyl complex $[Fe(CO)_4(C_4H_7)]^+ Cl^-$ is formed, which, on losing CO, is readily converted into tricarbonyl-(1-methyl-π-allyl)iron. The opinion in the literature as to the geometric configuration of this complex is divided. Impastato[81] and Heck and Boss[83] ascribe to the π-crotyl ligand the *anti*-configuration, whereas Murdoch and Weiss[82] consider the *syn*-form is correct.

When a benzene solution of the complex is boiled or the crystalline product is heated above its melting point (58–60°C), it decomposes to give $Fe(CO)_3(C_4H_6)$ and $FeCl_2$, with the simultaneous liberation of carbon monoxide and a mixture of butenes. The poor solubility of the complexes in water and their good solubility in organic solvents indicates the covalent nature of the bonding of the halogen with the metal.

The tricarbonyl-π-allyliron halides can be converted into salts containing the corresponding cations on treatment with $AgClO_4$ or $AgBF_4$,[84] for example, (VII)

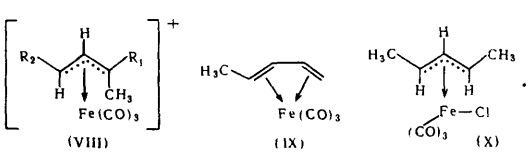


(VII)

The formation of cations proceeds without change in the configuration of the allyl ligand. The tricarbonyl-π-allyliron cationic complexes can also be obtained by treating tricarbonyldieneiron complexes in nitromethane solution with such acids as $HClO_4$, $HSbCl_6$, etc.[84,85]

Note that in the protonation of tricarbonylbutadieneiron, for example, with HBF_4, the tricarbonyl-(1-methyl-π-allyl)iron cation (VIII; $R_1 = R_2 = H$), having the opposite geometrical configuration to that of cation (VII), is formed.

The same behaviour is observed in the preparation of π-allyl complexes from tricarbonyl penta-1,3-dieneiron (IX).



(VIII) (IX) (X)

Study of the NMR spectrum of the chloride (X), produced when (IX) is treated with hydrogen chloride, showed that there is only one type of proton in the methyl groups. The salt obtained from (X) by reaction with $AgClO_4$, had an analogous NMR spectrum. On the other hand, in the complex made by reaction of (IX) with perchloric acid the protons of the methyl groups gave two doublets (7.86 and 8.35 τ)[85]. This feature suggests that here a complex of another configuration (VIII; $R_1 = H$, $R_2 = CH_3$) is formed

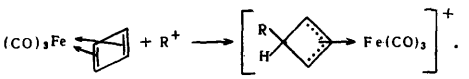
The fluoroborates of the tricarbonyl-(1,1-dimethyl-π-allyl)iron cation (VIII; $R_1 = CH_3$, $R_2 = H$) and the tricarbonyl-(1-methyl-3-phenyl-π-allyl)iron cation (VIII; $R_1 = H$, $R_2 = C_6H_5$) were obtained in a similar fashion from tricarbonyl-(2-methylbutadiene)iron and tricarbonyl-(1-phenylbutadiene)iron respectively.

Treatment of a salt of tricarbonyl-(1-methyl-π-allyl)-iron with water gives significant amounts of butan-2-one,

§ This reference appears to be entirely in error; the work referred to is to be found in Ref. 77 (Ed. of Translation).

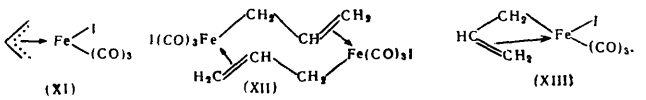
whereas pentan-2-one was obtained from the tricarbonyl-(1,3-dimethyl-π-allyl)iron salt.

A cationic complex analogous to (VII) but with a π-cyclobutenyl group was recently isolated by Fitzpatrik and coworkers[86] by the reaction of tricarbonylcyclobutadiene-iron with electrophilic reagents:



b. Reaction of Allyl Halides with Iron Carbonyls.

$Fe(CO)_5$. When pentacarbonyliron is heated with allyl iodide the reaction leads to the formation of tricarbonyl-π-allyliron iodide[87], but the analogous reactions with allyl chloride and bromide could not be affected[12,87]. Later, Heck and Boss[83] found a convenient method of obtaining tricarbonyl-π-allyliron complexes, by ultraviolet irradiation of pentane solutions of the allyl halide and $Fe(CO)_5$. The iodo-complexes can also be obtained by the exchange reaction of the corresponding chloro-complex with sodium iodide or lithium iodide in acetone solution[82,83]. In turn, the bromo- and chloro-complexes were obtained by exchange reaction from the iodo-complex and the corresponding tetra-alkylammonium salts in chloroform[88]. Plowman and Stone[87] suggested that the iodo-complex in solution consists of a mixture of monomer and dimer, and on the basis of spectra they gave the monomer formula (XI) and the dimer formula (XII) with bridging allyl groups.



(XI) (XII) (XIII)

However, Nesmeyanov and coworkers[88] consider that the differences observable in the proton magnetic resonance spectra of $Fe(CO)_3(C_3H_5)I$ and the usual π-allyl complexes can be explained by some distortion of delocalisation and approach to structure (XIII), but not by the presence of dimers.

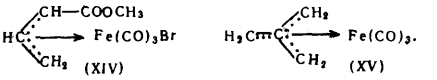
All the tricarbonyl-π-allyliron complexes react readily with triphenylphosphine, with replacement of one molecule of carbon monoxide by $(C_6H_5)_3P$,[83,88] but the product from π-$C_3H_5Fe(CO)_3Cl$ is extremely unstable, unlike its bromo- and iodo-analogues. According to Murdoch and Luncen[89] the loss of the halogen from the tricarbonylallyliron iodide in the presence of such anionic complexes as $[Mn(CO)_5]^-$ and $[(C_5H_5)Fe(CO)_2]^-$, and also its electrolytic reduction, takes place with the formation of the dimer of tricarbonyl-allyliron, which is readily split at the Fe–Fe bond to give a paramagnetic species $(C_3H_5)Fe(CO)_3$. Nesmeyanov and coworkers[88] detached the iodine from $[(C_3H_5)FeI(CO)_3]$ by treating it, in an inert atmosphere, with silver nitrate in nitromethane solution with the minimal quantity of methanol: this gave tricarbonylallyliron nitrate in 50% yield.

$Fe_2(CO)_9$. Allyl and 1-methylallyl halides react with $Fe_2(CO)_9$ at moderate temperatures, according to the equation[90]:

$$H_2C{=}CH{-}CH_2X + Fe_2(CO)_9 \rightarrow \pi\text{-}C_3H_5{-}Fe(CO)_3X + Fe(CO)_5 + CO.$$

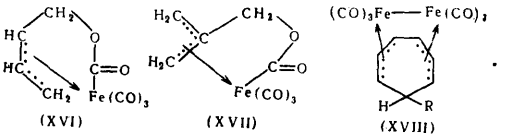
Similarly, methyl γ-bromocrotonate gave bromotricarbonyl-(1-methoxycarbonyl-π-allyl)iron (XIV), and 1,3- and 2,3-dibromoprop-1-ene gave the two isomeric bromotricarbonyl-(1-bromo-π-allyl)iron and bromotricarbonyl-(2-bromo-π-allyl)iron.

Reaction of 3-chloro-(2-chloromethyl)propene with $Fe_2(CO)_9$ for 12 h at room temperature leads to tricarbonyl-(trimethylenemethane)iron (XV)[91]. Protonation of the complex with strong acids, for example, 96% H_2SO_4, gives the tricarbonyl-π-methylallyliron cation, from which on further treatment with HCl the covalent chlorotricarbonyl-(π-methylallyl)iron was obtained.



(XIV) (XV)

A new type of compound was discovered by Murdoch[92], who observed that the product of the reaction of 4-chloro-but-2-en-1-ol and nonacarbonyldi-iron contained neither alcoholic nor chloro-groups. The same product, but in greater yield, was obtained from but-2-ene-1,4-diol and $Fe_2(CO)_9$. On the basis of chemical, analytical, and spectroscopic studies it was given the structure (XVI):

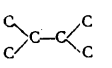


(XVI) (XVII) (XVIII)

The complex (XVII), isomeric to (XVI), was obtained from $Fe_2(CO)_9$ and 2-hydroxymethylprop-1-en-3-ol. Similar reactions of 2,3-dimethylbut-2-en-1,4-diol and hex-3-en-2,4-diol with $Fe_2(CO)_9$ led to the corresponding dimethyl derivative of complex (XVI). The reaction of (XVI) with triphenylphosphine gives a complex in which one CO group is replaced by a $(C_6H_5)_3P$ group.

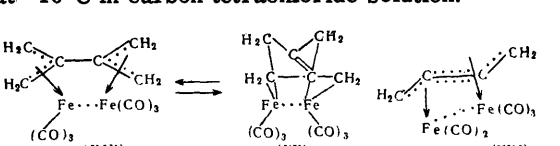
In reactions of $Fe_2(CO)_9$ with cycloheptatriene, 7-methoxy-cyclohepta-1,3,5-triene, cyclo-octa-1,3,5-triene[93], and cyclo-octatetraene[93–95], Pettit and coworkers always obtained orange-red crystalline complexes in which the $Fe_2(CO)_9$ grouping was attached to the corresponding cyclic diene. Investigation of the NMR and nuclear γ resonance [Mössbauer] spectra showed the equivalence of the two $Fe(CO)_3$ groups and it was therefore assumed that these compounds were new bis-(π-allylenironcarbonyl) complexes. Formula (XVIII) illustrates the structure of cyclopentatriene–$Fe_2(CO)_6$ (R = H) and its methoxy-derivative (R = OCH_3).

$Fe_3(CO)_{12}$. By the reaction of allene with $Fe_3(CO)_{12}$, Nakamura and coworkers[96] obtained a compound of composition $[(C_3H_4)Fe(CO)_3]_2$. From chemical investigations and studies of the infrared and NMR spectra it was found[97] that this compound has the skeleton



and is a second example of a bi-π-allylene compound.

Investigation of the NMR spectra of hexacarbonyl-(2,2′-bi-π-allylene)di-iron (XIX) showed[97] that the complex is in tautomeric equilibrium with a new complex of non-allyl type (XX); the equilibrium is established rather rapidly even at −10°C in carbon tetrachloride solution:



(XIX) (XX) (XXI)

The reaction of 1,4-dibromobut-2-yne, and also of 1,4-dichlorobut-2-yne or 1,4-diacetoxybut-2-yne, with $Fe_3(CO)_{12}$ in the presence of zinc dust at 60°C gave a red crystalline substance, $Fe_2(CO)_5(C_4H_4)$ [96,98]. The most probable structure for this compound is (XXI) with two π-allyl groupings arranged at an angle to one another.

c. Special Methods of Making π-Allyl Complexes of Iron

The σ-allyliron complexes $\pi\text{-}C_5H_5Fe(CO)_2\text{-}\sigma\text{-}C_3H_5$ and $\pi\text{-}C_5H_5Fe(CO)_2\text{-}\sigma\text{-}C_4H_7$, like the analogous molybdenum compounds, liberate one molecule of carbon monoxide under the action of ultraviolet radiation and are converted into the corresponding π-allyl complexes in high yields [18].

π-Allyl complexes of iron were recently obtained [99,100] with, in addition to carbonyl groups attached to the metal, one nitrosyl group. The carbonylnitrosylallyl complexes of iron are readily obtained from the corresponding sodium salts:

$$Na[Fe(CO)_3NO] + C_3H_5X \rightarrow NaX + \pi\text{-}C_3H_5Fe(CO)_2NO + CO.$$

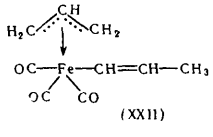
Complexes of this type can be obtained by the addition of $HFe(CO)_3(NO)$ to a conjugated diene, for example:

$$HFe(CO)_3NO + C_4H_6 \rightarrow \pi\text{-}C_4H_7Fe(CO)_2NO + CO.$$

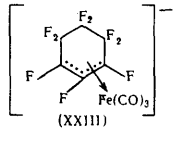
A method based on the reaction of halogenotricarbonyl-π-allyliron complexes or their phosphinic complexes with nitrogen(II) oxide has been proposed. A triphenylphosphine complex with a nitrosyl group can be obtained directly from $(C_4H_7)Fe(CO)_2(NO)$:

$$\pi\text{-}C_4H_7Fe(CO)_2NO + P(C_6H_5)_3 \rightarrow \pi\text{-}C_4H_7Fe(CO)(NO)[P(C_6H_5)_3] + CO.$$

Tris-(π-allyl)iron was obtained in 10–35% yield by the reaction of allylmagnesium chloride with iron(III) chloride or acetylacetonate at −80°C. [73,74,101] Reaction of trisallyliron with carbon monoxide at +10°C gives a compound which has been given the structure (XXII) on the basis of its infrared spectrum [23,101]:



(XXII)



(XXIII)

It is also reported [102] that tricarbonyl(perfluorocyclohexadiene)iron treated with caesium fluoride gives a caesium salt with a (π-perfluorocyclohexenyl)tricarbonylferrate anion (XXIII).

6. COBALT COMPLEXES

There are two main methods for preparing π-allyl complexes of cobalt.

a. Addition of Hydrocobalttetracarbonyl to Diene Hydrocarbons

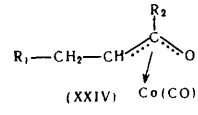
(1-Methyl-π-allyl)cobalttricarbonyl $Co(CO)_3(C_4H_7)$, obtained by Prichard [4] by the reaction of hydrogen tetracarbonylcobaltate(−1) with butadiene in isopropyl alcohol was, as mentioned above, the first π-allyl compound. $KCo(CO)_4$ [5] and $Co_2(CO)_8$ [10] can be used instead of $HCo(CO)_4$ if glacial acetic acid is used as the reaction medium. Aldridge and coworkers [6] showed that $Co(CO)_3(C_4H_7)$ is formed as a mixture of *syn* and *anti* forms in the ratio 6 : 4. The intermediate product in these reactions is the complex $Co(CO)_4(C_4H_7)$, which readily loses a molecule of carbon monoxide and is converted into tricarbonyl-1-methyl-π-allylcobalt [10].

The reactions of $HCo(CO)_4$ with 2-methylbuta-1,3-diene, penta-1,3-diene, and 2,3-dimethylbutadiene [32] proceed similarly. The reaction of penta-1,4-diene is accompanied by rearrangement of the alkadiene and leads to the formation of *syn* and *anti* isomeric forms of (1-ethyl-π-allyl)cobalttricarbonyl and of the 1,3-dimethyl complex. The yield of the latter does not exceed 10–15%. [103]

When the reaction is carried out under a pressure of carbon monoxide, some oxidation products, such as hex-5-enal and 2-methylcyclopentanone, [104,105] are formed as well as the (1-ethyl-π-allyl)cobalttricarbonyl. The yield of the complex decreases as the pressure is raised.

Addition of butadiene to the $[CoH(CN)_5]^{3-}$ ion gives the tetracyano-1-methyl-π-allylcobalt anion $[Co(CN)_4.(C_4H_7)]^{2-}$. [106,107] This process, as with hydrogen tetracarbonylcobaltate(−1), proceeds through the formation of the σ-allyl complex $[Co(CN)_5(C_4H_7)]^{3-}$.

When unsaturated aldehydes and ketones react with hydrogen tetracarbonylcobaltate(-1) under hydroformylation conditions the products are, according to the mechanism suggested by Goetz and Orchin [80], the so-called π-oxapropenyl complexes of type (XXIV). In this way the complex (XXIV; $R_1 = CH_3$, $R_2 = H$) was obtained from but-2-enal and the more stable complex (XXIV; $R_1 = H$, $R_2 = CH_3$) from butenone.

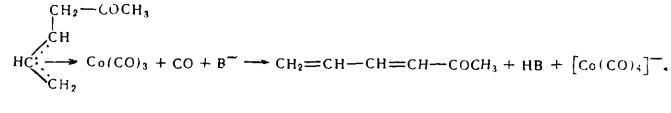


(XXIV)

Heck [108,109] found a way of obtaining substituted π-allyl complexes with an acyl group in the side-chain. These products are formed in the reaction of butadiene, $NaCo(CO)_4$, and alkyl or acyl halides in ethereal solution. The rate of the process depends on the reactivity of the halide. Tetracarbonylacylcobalt and tetracarbonylalkylcobalt complexes are formed in the first stage of the reaction, and then, by reaction with butadiene, are converted into active tricarbonylacylcobalt complexes.

1-Substituted tricarbonyl-π-allylcobalt complexes, obtained in the reaction of dienes with tetracarbonylalkylcobalt or tetracarbonylacylcobalt complexes, exist in *syn* and *anti* forms. For example, the complex from tetracarbonylmethylcobalt and *cis*-penta-1,3-diene is found in the *syn*, and that from 2,3-dimethylbutadiene, in the *anti* configuration. π-Allyl complexes have also been obtained by reactions with 2-methylbutadiene, 4-methylpenta-1,3-diene, and *trans*-1-methoxybutadiene in methyl sorbate [108].

The structure of the complexes formed was studied using their reactions with bases (dicyclohexylethylamine, sodium methoxide, or potassium t-butoxide) in the presence of carbon monoxide [110]. The bases evidently detach a proton from the α-methylene group (in relation to the carbonyl), which leads to the liberation of a tricarbonylcobalt group; this adds CO and forms a stable tetracarbonylcobaltate anion, for example:



On reaction with $CH_3Co(CO)_4$ and a base, *cis*-penta-1,3-diene gives

$$CH_3—CO—C(CH_3)=CH—CH=CH_2,$$

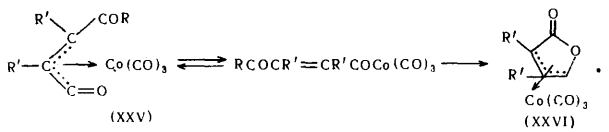
but *trans*-penta-1,3-diene gives:

$$CH_3—CO—CH=CH—CH=CH—CH_3.$$

When disubstituted acetylene is used instead of a diene in the reaction with a carbonylacylcobalt complex, then from the intermediate complex

$$C—R—CO—CR'=CR'—COCo(CO)_3,$$

which is essentially mainly in the form of a π-acrylic complex (XXV), a 2,3-dialkyl-π-(2,4-penteno-4-lactonyl)cobalttricarbonyl complex (XXVI) is obtained [111]:



(XXV) (XXVI)

As Heck has shown [112], the addition of acyl or alkyl tetracarbonylcobaltates(-1) to $\alpha\beta$-unsaturated aldehydes and ketones leads to tricarbonyl-(1-acyloxy-π-allyl)cobalt complexes, the triphenylphosphine derivatives of which have been characterised.

The carbonyl-π-allyl complexes of cobalt are usually characterised as their triphenylphosphine derivatives, which are more stable. The reaction of $Co(CO)_3(C_3H_5)$ with $(C_6H_5)_3P$ is accompanied by the formation of yellow crystalline dicarbonyl-π-allyltriphenylphosphinecobalt and the liberation of carbon monoxide. [113-115] Kinetic investigations showed that the rate of this reaction is independent of the phosphine concentration when the latter exceeds 0.06 M. [114] The replacement of the hydrogen atom at the central carbon atom of the π-allyl group by electron-donating or electron-accepting groups increases the reaction rate. On the other hand, replacement of a hydrogen atom at the first or third carbon atoms of the π-allyl group by an electron-accepting substituent decreases the reaction rate by a factor of almost 30. [112]

Tetracarbonyl-σ-allylcobalt reacts differently with triphenylphosphine [113-115]. Liberation of carbon monoxide is not observed but an acyl complex is formed:

$$CH_2=CH—CH_2COCo(CO)_3P(C_6H_5)_3$$

tricarbonyl(but-3-enoyl)(triphenylphosphine)cobalt, which can also be obtained by the reaction of allyl bromide with $NaCo(CO)_4$ and CO in the presence of triphenylphosphine.

In the reaction with triphenylphosphine as unusual type of metal–organic bond is clearly evident in the tricarbonyl-π-allylcobalt complexes, since compounds with a σ-bond (tetracarbonylalkylcobalt complexes) give acylcobalt derivatives with $(C_6H_5)_3P$ [115] but the cyclo-octatetraene ligand is displaced from a π-complex, tricarbonylcyclo-octatetraenecobalt [116].

The reaction of π-allylcobalttricarbonyl complexes with trimethylolpropan phosphite [? trimethylene propenyl phosphite (Ed. of Translation)] has been shown by Heck [117] to proceed by replacement of two molecules of carbon monoxide:

$$C_3H_5Co(CO)_3 + 2\,PO_3C_6H_{11} \rightarrow C_3H_5Co(CO)(PO_3C_6H_{11})_2 + 2\,CO.$$

Bis(trimethylolpropan phosphite) derivatives were also obtained from 2-chloro-π-allyl-, 1-acetyl-π-allyl, and 1-benzoylmethyl-3-methoxy-π-allyl-tricarbonylcobalt complexes.

All these compounds are crystalline, from yellow to orange in colour, and fairly stable in air.

b. Reaction of the $[Co(CO)_4]^-$ Anion with Allyl Halides

This method was used to make tricarbonyl-π-allylcobalt [9,10,113,114], and the 1-methyl- [9,10,113], 1- and 2-chloro- [10], 2-methyl-, 2-bromo-, 2-phenyl-, and 1-methoxycarbonyl- [114] π-allyltricarbonylcobalt complexes from allyl and 1-methylallyl halides, 2,3- and 1,3-dichloropropene, 2-phenylallyl bromide, and methyl 3-bromocrotonate respectively. The reaction was carried out with a slight excess of $KCo(CO)_4$ or $NaCo(CO)_4$.

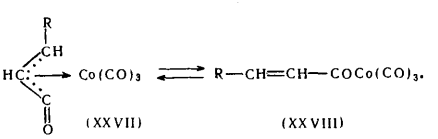
When there is an excess of the allyl halide, for example, C_3H_5Br, the reaction proceeds in another direction:

$$2\,C_3H_5Co(CO)_3 + 4\,C_3H_5Br \rightarrow 3\,C_6H_{10} + 2\,CoBr_2.$$

Tricarbonyl-π-allylcobalt complexes are also readily obtained by decomposition of acyl tetracarbonylcobaltates formed in the reaction of $NaCo(CO)_4$ with allyl halides in the presence of carbon monoxide [9,113,118]:

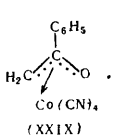
$$NaCo(CO)_4 + CH_2=CH—CH_2Cl + CO \xrightarrow{-NaCl} CH_2=CH—CH_2COCo(CO)_4 \xrightarrow{-2Co} \rightarrow C_3H_5Co(CO)_3.$$

When vinylacetyl chloride is used instead of allyl halides the reaction proceeds in the absence of carbon monoxide [9,113]. The reaction of $NaCo(CO)_4$ with acrylyl, crotonyl, or sorbyl chloride in the presence of carbon monoxide leads to the formation of an equilibrium mixture of π-acrylyl complexes (XXVII) and acyl complexes (XXVIII) [113,119,120]. On adding triphenylphosphine a complex of (XXVIII) with one molecule of $(C_6H_5)_3P$ was isolated:



(XXVII) (XXVIII)

π-Allyl anions with cyano-groups, already mentioned above, can also be obtained by the reaction of allyl halides with the pentacyanocobaltate(II) anion $[Co(CN)_5]^{3-}$. [106,107] The reaction of pentacyanocobaltate(II) with phenacyl bromide led to a complex which was given a structure of the π-oxapropenyl type (XXIX).

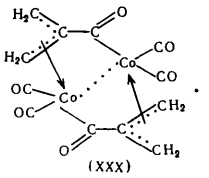


(XXIX)

In addition to these two general methods for the prepartion of π-allyl complexes of cobalt, some other synthetic routes must be noted.

Carbonyl-π-allyl-π-cyclopentadienylcobalt bromide was made by the reaction of allyl bromide with $Co(CO)_2(C_5H_5)$ [121]. Heck [122] showed that in this reaction not only $[Co(CO)(C_3H_5).(C_5H_5)]Br$ but also a little π-allyl-π-cyclopentadienylcobalt bromide is formed. With allyl iodide the main product was also an ionic complex, but more of the covalent $CoI(\pi\text{-}C_3H_5)(C_5H_5)$ was present (10%). With allyl chloride only carbonyl-π-allyl-π-cyclopentadienylcobalt chloride is formed. The treatment of a benzene solution of octacarbonylcobalt with allene at 40°C leads to a carbonyl-π-allylacylcobalt complex (XXX) [123], the structure of which

was established on the basis of NMR and infrared spectra, and by bromination.

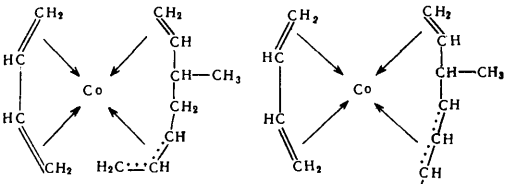


(XXX)

Tris-(π-allyl)cobalt $(C_3H_5)_3Co$ was obtained by the reaction of an ethereal solution of allylmagnesium chloride and cobalt acetylacetonate at −80°C (yield 45–50%)[73,74]. With cobalt chloride the yield did not exceed 20%. The compound is thermally unstable and decomposes rapidly, even at 0°C.

There are indications that the reaction of $(C_3H_5)_3Co$ with hydrogen halides leads to the formation of bis-(π-allyl)-cobalt halides[65]. The product of the reaction of $(C_3H_5)_3Co$ with CO at −35°C is π-allylcobalttricarbonyl[23].

By the reaction of an ethanol solution of $CoCl_2$ with sodium tetrahydroborate in the presence of butadiene Natta and coworkers[124] obtained a complex of composition $CoC_{12}H_{19}$, to which they ascribed one of the following structures:



(XXXI) (XXXII)

The compound melts at ~ 37°C, dissolves in hydrocarbons with the formation of red solutions, and is insoluble in water. On reaction with carbon monoxide two tricarbonyl-π-allyl complexes were isolated: $(C_4H_7)Co(CO)_3$ and $(C_8H_{13})Co(CO)_3$. The latter, in turn, was made from $Co_2(CO)_8$ and 3-methyl-hepta-1,4,6-triene in acetic acid solution.

7. NICKEL COMPLEXES

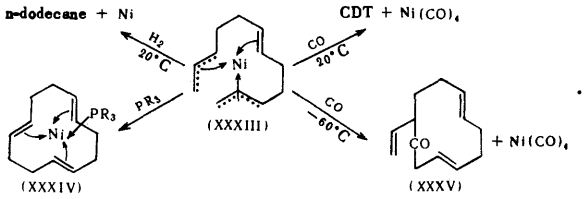
The following types of π-allyl complexes of nickel are known: bis-(π-allyl), bis-(π-allylnickel halides), π-allyl-π-cyclopentadienyl, and also complexes with cyclic π-allyl ligands.

a. Bis-(π-Allyl) Complexes

The simplest complex of this class, bis-(π-allyl)nickel, $(C_3H_5)_2Ni$, was first obtained by Wilke[23,29,125-128] by the reaction of an ethereal solution of allylmagnesium chloride with anhydrous nickel bromide at −10°C. 1-Methylallyl, 2-methylallyl, and phenylallyl complexes were obtained in a similar manner[73,74,129,130]. $(C_3H_5)_2Ni$ is readily soluble in hydrocarbons and stable in relation to water. It ignites in air. On reduction with hydrogen it liberates propane and metallic nickel is left. The reaction of $(C_3H_5)_2Ni$ with compounds which exhibit electron-donating properties is accompanied by the formation of biallyl. In addition to biallyl, in the presence of carbon monoxide or triphenylphosphine, nickelcarbonyl and $[(C_6H_5)_3P]_4Ni$ is formed[125,126,128].

Under certain conditions and at reagent ratios of 1 : 1 for bis-(1-methyl-π-allyl)nickel and bis-(2-methyl-π-allyl)-nickel their addition product with triphenylphosphine of composition $Ni(\pi\text{-}C_4H_7)(\sigma\text{-}C_4H_7).[P(C_2H_5)_3]$ was isolated[23,129].

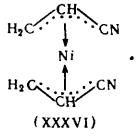
Wilke and coworkers[128,131] obtained compounds of general formula $C_{12}H_{18}Ni$ as an intermediate product in the preparation of cyclododecatriene (CDT) from butadiene. On the basis of the infrared spectra this complex was assigned structure (XXXIII) in which three molecules of butadiene form a chain of 12 carbon atoms with a *trans* double bond and two allyl groupings:



(XXXIV) (XXXIII) (XXXV)

Reaction of (XXXIII) with electron donors (carbon monoxide, phosphine, butadiene) leads to ring closure, and when phosphine is used detachment of the cyclododecatriene does not take place (XXXIV). With carbon monoxide at −60°C the reaction is quite different, tetracarbonylnickel and vinylcycloundecadiene (XXXV) being formed. When hydrogen reacts with (XXXIII) n-dodecane is formed[125,128,131].

According to Schrauzer[132], complexes of nickel with acrylonitrile (XXXVI), acrolein, cinnamonitrile, and fumaronitrile, which are obtained by the reaction of tetracarbonylnickel with corresponding unsaturated compounds, can be classified as π-allyl complexes:



(XXXVI)

b. Bis-(π-Allylnickel Halides)

Bis-(π-allylnickel halides) are obtained by the reaction of tetracarbonylnickel with allyl halides[12,52,57]:

$$2\,Ni(CO_4) + 2\,RX \rightarrow [RNiX]_2 + 8\,CO.$$

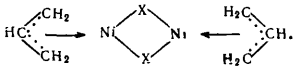
Benzene is the most suitable solvent for this reaction[12].

The reaction of tetracarbonylnickel with allyl halides in an alcoholic medium leads to the dimerisation of the allyl residues[133]. Thus, hexa-1,5-diene is obtained from allyl halides and octa-2,6-diene (7.8%) and 3-methylhepta-1,5-diene (22%) from a mixture of crotyl chloride and 3-chloro-but-1-ene.

Both in the dimerisation and in the formation of π-allyl complexes, the reaction evidently proceeds through the formation of an intermediate compound, $R-[(C_3H_4)NiX(CO)]$[35,134].

Bis-(π-allylnickel halides) can also be obtained by the reaction of allyl halides with other complexes of nickel(0), such as bis(cyclo-octadiene)nickel(0), cyclododecatriene-nickel[135] or by reaction of bis-(π-allyl) complexes of nickel with hydrogen halides in ethereal solution at −80°C[65,129].

According to Fischer and Bürger [12,52,57] bis-(π-allylnickel halides) have structure (XXXVII) with halogeno-bridges.



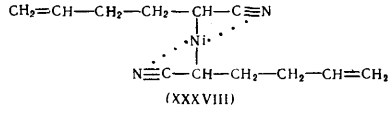
(XXXVII)

They are readily soluble in organic solvents to give dark red solutions. In water saturated with nitrogen bis-(π-allylnickel halides) form orange-red solutions which are stable for a short time but which decompose on long standing, with the formation of metallic nickel.

Chiusoli and Merzoni [136] found that during the carbonylation of methanol solutions of $(C_3H_5NiBr)_2$ methyl vinylacetate is formed. A mixture of acetylene and carbon monoxide acts on $(NiXC_3H_5)_2$ to give, in addition to tetracarbonylnickel, derivatives of hexa-2,5-dienoic acid, depending upon the nature of the solvent; for example, in ether at ~ 0°C the following reaction takes place [137]:

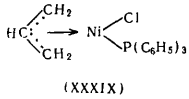
$$(C_3H_5NiBr)_2 + 10\,CO + 2\,C_2H_2 \rightarrow 2\,CH_3{=}CH{-}CH_2{-}CH{=}CH{-}COBr + 2\,Ni(CO)_4.$$

The reaction of bis-(π-allylnickel bromide) with methyl acrylate in benzene solution at room temperature leads to the formation of methyl hexa-2,5-dienoate and methyl hex-5-enoate [138,139]. Acrylonitrile reacts with $(C_3H_5NiBr)_2$ with the separation of a complex which has been given the structure (XXXVIII):



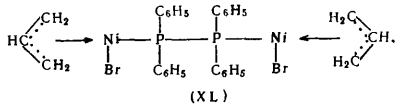
(XXXVIII)

The reaction of bis-(π-allylnickel halides) with triphenylphosphine leads to the breaking of the halogeno-bridges [23,29,140]. The complexes thus formed (XXXIX):



(XXXIX)

were also obtained by the reaction of allyl chloride with $Ni(CO)_3[P(C_6H_5)_3]$ [141]. The reaction of tetraphenyldiphosphinedinickelhexacarbonyl [μ-(tetraphenyldiphosphenylene)bis(tricarbonylnickel)(Ed. of Translation)] with allyl bromide leads to the π-allyl complex (XL) with a diphosphinic bridge [142]:



(XL)

Bogdanović and coworkers [140] obtained π-allylmethylnickel by the reaction of $(C_3H_5NiBr)_2$ with methylmagnesium chloride in ether (-78°C). This product is extremely unstable and even at -60°C it changes into bis-(π-allyl) nickel. π-Allylmethylnickel-triphenylphosphine was made in a similar fashion from complex (XXXIX).

Wilke and coworkers [28] obtained bis-(π-allylnickel cyanide) in methanol starting from $(C_3H_5)_2Ni$ and HCN or $(C_3H_5NiBr)_2$ and KCN.

c. π-Allyl-π-Cyclopentadienyl Complexes of Nickel

π-Allyl-, and also 1-methyl-π-allyl-π-cyclopentadienyl complexes of nickel are obtained from the corresponding bis-(π-allylnickel halides) and cyclopentadienylsodium [12,52]:

$$(C_3H_5NiBr)_2 + 2\,NaC_5H_5 \rightarrow 2\,C_3H_5NiC_5H_5 + 2\,NaBr.$$

In addition, the same products are obtained by the reaction of bis-(π-cyclopentadienylnickel) with the corresponding allylmagnesium halides [10,143], for example:

$$C_3H_5MgCl + (\pi\text{-}C_5H_5)_2Ni \rightarrow C_5H_5MgCl + C_3H_5NiC_5H_5.$$

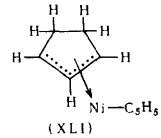
1-methyl-π-allyl-π-cyclopentadienylnickel was also obtained by the reaction of $(C_5H_5)_2Ni$ with butadiene and consisted of a mixture of *syn*- and *anti*-isomers [144]. The reaction of 1-methylallyl chloride with the potassium salt of π-cyclopentadienylnickelcarbonyl leads to the formation of the same complex [144]:

$$C_4H_7Cl + K[C_5H_5NiCO] \rightarrow C_4H_7NiC_5H_5 + CO + KCl.$$

All the π-allyl-π-cyclopentadienyl complexes of nickel are readily soluble in most organic solvents. These compounds rapidly decompose in air. Cryoscopic measurements in benzene have shown that the complexes have a monomeric structure.

d. Complexes with Cyclic π-Allyl Ligands

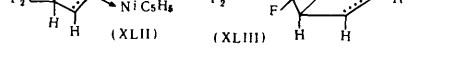
A π-allyl complex of nickel with a cyclic ligand was first obtained by Fischer and Werner [53,145] by the reaction of tetracarbonyl nickel with cyclopentadiene in n-hexane solution. However, it was incorrectly given the structure of bis(cyclopentadiene)nickel, $(C_5H_6)_2Ni$. [53] It was later found, from infrared and NMR spectra, that this compound is a π-cyclopentadienyl-π-cyclopentenyl complex (XLI) [1,17,146-150].



(XLI)

Dubeck and Filbey [149] prepared it by reduction of $(C_5H_5)_2Ni$ with sodium amalgam in methanol solution, and also by the reaction of cyclopentenylmagnesium bromide, C_5H_5Na, and anhydrous $NiBr_2$ at -10°C.

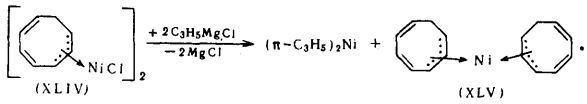
Reaction of bis-(π-cyclopentadienyl)nickel with tetrafluoroethylene gave a π-allyl complex of structure (XLII), which was proposed on the basis of an examination of the ^1H- and ^{19}F-NMR spectra [151]. Complexes analogous to (XLII) were also obtained by the reaction of $(C_5H_5)_2Ni$ with chlorotrifluoroethylene and hexafluorobut-2-yne [149,151]. The product of the reaction of $(C_5H_5)_2Ni$ with octafluorocyclohexa-1,3-diene was represented as the π-allyl complex (XLIII) on the basis of spectroscopic data [152]:



(XLII) (XLIII)

Nickel compounds with cyclobutenyl [39,40,153-157] and cyclopropenyl [158,159] ligands must also be classified as complexes of the π-allyl type. A series of cyclic π-allyl nickel complexes has been isolated in Wilke's laboratory [23,129]—bis-(π-cyclohexenyl)nickel, bis-(π-cycloheptenyl)nickel, bis-(π-cyclo-octenyl)nickel, and also the corresponding π-enylnickel chlorides formed from them on treatment with HCl. The reaction of cyclo-octatetraenylnickel with HCl

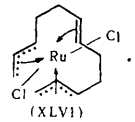
at −80°C in toluene gave red crystals of bis-(π-cyclo-octatrienylnickel chloride) (XLIV)[23], which when treated with allylmagnesium chloride yielded bis-(π-cyclo-octatrienyl)nickel (XLV) and bis-(π-allyl)nickel, instead of the expected π-allyl-π-cyclo-octatrienylnickel:



(XLIV) (XLV)

8. COMPLEXES OF RUTHENIUM, RHODIUM, AND IRIDIUM

Two π-allyl complexes of ruthenium are known at present. Complex (XLVI) was obtained by the reaction of ruthenium(III) chloride and butadiene in 2-methoxyethanol solution at 100°C.[160,161] It is a monomer in benzene. Complexes of rhodium and iridium with butadiene were obtained in the same way.



(XLVI)

The reaction of $RuCl_3$ in alcoholic solution with 2-methylbuta-1,3-diene leads to the formation of the dimeric dichloro-(2,7-dimethylocta-2,6-dien-1,8-ylene)ruthenium, to which Porri and coworkers[162] ascribed a π-allyl structure.

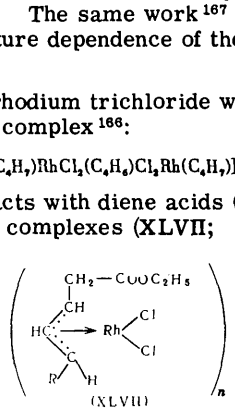
The diamagnetic cyclododeca-1,5-dienylrhodium dichloride, the first π-allyl complex of rhodium(III), was obtained by Paiaro and coworkers[163,164] from $RhCl_3.3H_2O$ and cyclododeca-*trans*-1,*trans*-5,*trans*-9-triene in boiling ethanol. The polymeric nature of the substance is shown by its insolubility in the usual organic solvents, and its ability to dissolve in dilute ammonia and to react with Lewis bases (CO, amines, alkenes) with the formation of monomeric complexes $C_{12}H_{19}RhCl_2B$, where B is the base.

Dimeric bis-(π-allyl)rhodium chloride was prepared by Shaw and coworkers[165] by the reaction of $[RhCl(CO)_2]_2$ with allyl chloride in methanol containing a little water. The reaction of the complex with pyridine, thallium(I) acetylacetonate, and cyclopentadienylthallium led to the corresponding monomeric compound. Treatment of $[(\pi\text{-}C_3H_5)_2RhCl]_2$ with allylmagnesium chloride gives trisallylrhodium[166], which was also obtained by the reaction of anhydrous $RhCl_3$ with C_3H_5MgCl at 0°C.[167] The same work[167] also gave information on the temperature dependence of the NMR spectra of $(C_3H_5)_3Rh$.

The reaction of rhodium trichloride with butadiene in ethanol leads to the complex[166]:

$$[(C_4H_7)RhCl_2(C_4H_6)Cl_2Rh(C_4H_7)].$$

$RhCl_3.3H_2O$ also reacts with diene acids (sorbic, vinylacrylic) to form the complexes (XLVII; R = H, CH_3)[168]:



(XLVII)

Corresponding monomeric complexes were obtained from (XLVII) with 2,2-bipyridyl, ethylenediamine, or carbon monoxide.

π-Allyl-π-cyclo-octa-1,5-dienerhodium was made by the reaction of $[C_8H_{12}RhI]_2$ with an excess of allylmagnesium bromide at 0°C.[169]

Wilkinson and coworkers[170] recently reported the preparation of the complexes

$$R—C_3H_4RhCl_2[PC_6H_5)_3],$$

the NMR spectra of which were studied by Volger and Vrieze[30].

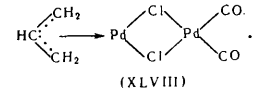
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9. PALLADIUM COMPLEXES

A. Preparation

a. Reactions with allyl halides. Yellow bis-(π-allylpalladium bromide) is obtained when palladium sponge is heated with allyl bromide[12,56]. However, in experiments with allyl chloride and iodide, and also with crotyl bromide, π-allyl palladium compounds were not obtained.

The reaction of a solution of allyl chloride in 50% acetic acid with palladium chloride at 30°C leads to the formation of bis-(π-allylpalladium chloride)[171,172]. At room temperature methylallyl chloride gives a red complex sparingly soluble in organic solvents, $(C_4H_8PdCl_2)_2$. When this is boiled in water it decomposes to metallic palladium and bis-(π-methylallylpalladium dichloride). Dent and coworkers[33] found that these complexes can be obtained almost quantitatively by the action of carbon monoxide on a mixture of Na_2PdCl_4 and allyl chlorides in methanol at atmospheric pressure and room temperature. In the presence of palladium and calcium chlorides in addition to π-allylchloride complexes of palladium a compound insoluble in the usual organic solvents could be isolated, to which the authors ascribed the structure (XLVIII) on the basis of the infrared spectra.



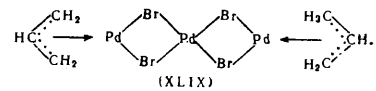
(XLVIII)

Subsequently Shaw and coworkers[173] showed that in the absence of CO and H_2O allylpalladium chloride cannot be prepared by Dent's method.

b. Reactions with allyl alcohol, alkenes and acetylenes. Bis-(π-allylpalladium chloride) was first obtained independently by Syrkin and coworkers[7] and by Smidt and Hafner[8,174] by the reaction of palladium chloride with allyl chloride in acid medium at room temperature.

Dimeric $(C_3H_5PdCl)_2$ is a yellow crystalline substance readily soluble in polar solvents and also in dilute aqueous acids and alkalis. The report by Syrkin and coworkers[7] on the preparation of a second dark green form of $(C_3H_5PdCl)_2$ at temperatures below 10°C was not confirmed in work by other investigators[175].

When allyl alcohol reacts with $PdBr_2$ in hydrobromic acid solution under the same conditions, bis-(π-allylpalladium bromide) is formed[176]. On increasing the $PdBr_2$ concentration a complex of composition $C_6H_{10}Pd_3Br_4$ is also formed, for which structure (XLIX) has been proposed:



(XLIX)

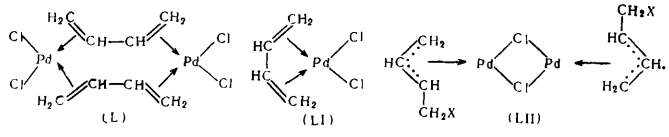
The reaction of alkenes with various palladium compounds (for example, $PdCl_2$, Na_2PdCl_4, and $[PdCl_2(C_6H_5CN)_2]$) is a most general and convenient method for obtaining π-allyl complexes of palladium.

For most alkenes the reaction with palladium chloride passes through the stage of formation of π-complexes of the type $[(alkene)PdCl_2]_2$, which lose HCl at a higher temperature, being changed into π-allyl complexes. Raising the reaction temperature to 50–100°C allows the π-allyl complexes to be obtained directly.

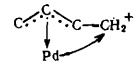
The Table gives the complexes prepared from the corresponding alkenes.

In the reaction of propene with an acetic acid solution of $PdCl_2$ saturated with sodium acetate a yellow complex of composition $C_6H_{11}PdCl$ is formed [180]. Study of the chemical properties and infrared and NMR spectra of the product showed that it is bis-(3-*syn*-ethyl-1-*syn*-methyl-π-allylpalladium chloride) [181]. The same complex is produced in the reaction of hex-1-ene with $PdCl_2$.

Some π-allyl complexes can be obtained by treatment of bis(benzonitrile)palladium chloride with dienes. The product of the reaction with butadiene was earlier given the structures (L, LI) [182-184]. However, Shaw [185] showed that butadienepalladium chloride is a π-allyl complex with halogen bridges (LII; X = Cl). Recently Donati and Conti [186] obtained the π-complex $(C_4H_6PdCl_2)_2$ by the reaction of butadiene with $(n\text{-}C_5H_{10}PdCl_2)_2$ at −40°C. At temperatures above −20°C the complex is converted into a π-allyl complex (LII; X = Cl).



Treatment of (LII) with methanol converts it into the less stable methoxy-derivative (LII; X = OMe). The methoxy- and also the ethoxy-π-crotylpalladium complexes are best obtained by passing butadiene into an alcoholic suspension of $Na_2[PdCl_4]$. Hence it is possible to obtain complexes from a large number of 1,3-dienes, such as 2-methylbutadiene, 4-methylpentadiene, 2,3-dimethylbutadiene, 2,4-dimethylpenta-1,3-diene, 1,1,4,4-tetramethylbutadiene, sorbic acid, and methyl sorbate [36,185,187]. It was also found [36] that methoxy-π-allyl palladium chloride treated with an ethanol solution of hydrogen chloride readily forms the corresponding ethoxy-derivative. The authors suggest the intermediate formation of a carbonium ion of type

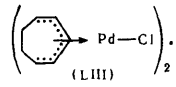


the considerably stability of which was explained (by analogy with the stability of α-ferrocenylcarbonium ions) by the participation of the palladium atom in the stabilisation of the neighbouring cationic centre.

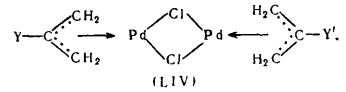
Cycloalkenes also react with palladium salts: cyclohexene [172,188], cycloheptene [188], cyclododecene [189], and their methyl derivatives, and also methylcyclo-octene [189]. The yields of the complexes increase with the number of carbon atoms in the ring, and here π-alkene complexes are formed initially, which are converted into π-allyl complexes with various degrees of ease. It has been noted [188], however, that cyclopentene gives a stable alkene complex which is not converted into a π-allyl compound. π-Allyl complexes are formed much more readily in the reaction of palladium salts with cyclic 1,3-dienes [190-192].

Robinson and Shaw [37] obtained dimeric methoxy-π-cyclohexenylpalladium chloride from cyclohexa-1,3-diene at room temperature. The stability of the product was much less than that of the corresponding acyclic complex [36].

A complex of composition $(C_7H_9PdCl)_2$ was obtained from cyclohepta-1,3-diene, and on the basis of the infrared spectra Robinson and Shaw [37] gave it the formula (LIII), where the palladium atom is associated with five atoms of the cycloheptadienyl ligand, as occurs in the π-cyclopentadienyl complexes.



π-Allyl complexes have also been obtained by passing allene or methyl-, dimethyl-, or tetramethyl-allenes through a methanol suspension of $Na_2[PdCl_4]$ [14,187]. The π-allyl complexes isolated had substituents at the central carbon atom of the π-allyl group $\left(\text{LIV; } Y = Y' = -C\begin{matrix}=CH_2\\ CH_2Cl\end{matrix}\right)$.



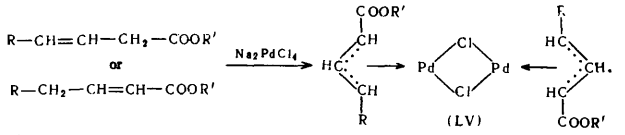
However, when allene is introduced into a methanol solution of dichlorobis(benzonitrile)palladium(II), then in addition to the above product about the same amount of the methoxy-derivative $\left(\text{LIV; } Y = Y' = -C\begin{matrix}=CH_2\\ CH_2OCH_3\end{matrix}\right)$ [193] is formed; the 2-methoxy-derivative is not formed. The reaction of $[PdCl_2(C_6H_5CN)_2]$ with allenes can also be effected in benzene or benzonitrile solutions [194]. The nature of the products formed depends on the method of preparation. When allene is introduced into a benzene solution of dichlorobis-(benzonitrile)palladium(II) the product is bis-(2-chloro-π-allylpalladium chloride) (LIV; Y = Y′ = Cl). In benzonitrile solution this complex with two 1-(chloromethyl)vinyl substituents at the central carbon atom in the π-allyl group is

TABLE. Bis[dichloro(π-allyl)palladium(II)] complexes

Initial alkene	Organic residue of the π-allyl complex	Reference
2-Methylpropene	2-methyl-π-allyl	172,177
2-Methylbut-1-ene 2-Methylbut-2-ene	1,2-dimethyl-π-allyl	177,178
2-Methylpent-1-ene 2-Methylpent-2-ene	1-ethyl-2-methyl-π-allyl	177,178
3-Methylpent-2-ene	1,2,3-trimethyl-π-allyl	177
2,3-Dimethylbut-1-ene 2,3-Dimethylbut-2-ene	1,1,2-trimethyl-π-allyl	177,178
2-Methylhex-2-ene	2-methyl-1-propyl-π-allyl	177
3-Ethylpent-2-ene	2-ethyl-1,3-dimethyl-π-allyl	177
2,4-Dimethylpent-2-ene	1-isopropyl-2-methyl-π-allyl	177
2,5-Dimethylhex-2-ene	1-isobutyl-2-methyl-π-allyl	177
2,4,4-Trimethylpent-1-ene (di-isobutene)	2-neopentyl-π-allyl	172,1
2,4,4-Trimethylpent-2-ene (di-isobutene)	1-t-butyl-2-methyl-π-allyl	177
Tri-isobutene (mixture of isomers)	mixture of isomers of composition $(C_{12}H_{21}PdCl)_2$	172
α-Methylstyrene	2-phenyl-π-allyl	172,179
β-Methylstyrene	1-phenyl-π-allyl	172
$\alpha\beta$-Dimethylstyrene	1-methyl-1-phenyl-π-allyl or 2-phenyl-1-methyl-π-allyl	172
Methylstilbene	1,2-diphenyl-π-allyl	172

obtained. On addition of solid $[PdCl_2(C_6H_5CN)_2]$ to a benzene solution of allene a mixed complex was obtained (LIV; Y = Cl, Y' = $-C\begin{matrix}CH_2\\CH_2Cl\end{matrix}$). The mechanism of the above reactions of allene hydrocarbons has been discussed by Heck[195] and Schultz[193].

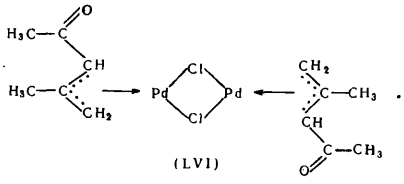
A π-allyl complex with an alkoxycarbonyl group at a terminal carbon of the allyl group was obtained in the reaction of $\alpha\beta$- or $\beta\gamma$-unsaturated carboxyl-containing esters with an alcoholic solution of $Na_2[PdCl_4]$[196]:



(LV)

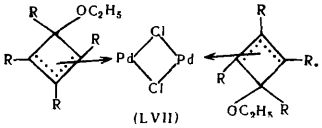
A compound of type (LV) can also be obtained by heating esters in the presence of palladium chloride or by adding the esters to a benzene solution of dichlorobis(benzonitrile)palladium(II).

A complex with a carbonyl group was first observed by Syrkin and coworkers[7] in the reaction of palladium chloride with mesityl oxide. Parshall and Wilkinson[197] showed that the complex has the structure (LVI) and is better obtained from $Na_2[PdCl_4]$:



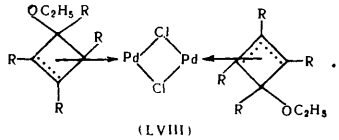
(LVI)

Mention must also be made of the complexes of palladium with four-membered cyclic π-allyl ligands. Such complexes can be obtained by the reaction of diphenylacetylene with alcoholic solutions of $PdCl_2$, $Na_2[PdCl_4]$, or $[PdCl_2(C_6H_5CN)_2]$[198-203], an orange-red complex of composition $C_{30}H_{25}OPdCl$ always being formed. Guy and Shaw[204] proposed for it a π-cyclobutenyl structure (LVII):



(LVII)

On treating the complex with hydrochloric acid a tetraphenylcyclobutadiene complex is obtained, $[(C_6H_5)_4C_4PdCl_2]$[199,200,202,204], from which treatment with ethanol gave an insoluble yellow substance of the same composition as complex (LVII) but with somewhat different chemical and physical properties. X-Ray diffraction examination, by Dahl and Oberhansli[39,40,205], confirmed the structure proposed by Guy and Shaw (LVII) and showed that both complexes are geometrical isomers (*exo*- and *endo*-), differing in the arrangement of the ethoxy-group in the cyclobutenyl ring. The complex obtained from tetraphenylcyclobutadiene palladium dichloride is the dimeric di-μ-chlorobis-(1-*exo*-ethoxy-1,2,3,4-tetraphenylcyclobutenylpalladium) (LVIII: R = C_6H_5).



(LVIII)

A substance with hydroxo groups was obtained on treating a dimethylformamide solution of $[(C_6H_5)_4C_4PdCl_2]$ with water[206].

In addition to diphenylacetylene, the compounds dichloro-(diphenylacetylene) and methylphenylacetylene react with palladium compounds, for example, $[PdCl_2(C_6H_5CN)_2]$[204,207].

The preparation of π-cyclopentadienylethoxy-π-tetraphenylcyclobutenylpalladium[157,208] and of a complex with the triphenylcyclopropenyl ligand[209] has been reported.

c. Reaction with allyl Grignard compounds. On mixing a benzene solution of chlorobis-(benzonitrile)palladium with 150% excess of an ethereal solution of allylmagnesium chloride, a bright yellow substance of composition $(C_6H_5CN)(C_3H_5)PdCl$ is formed. It is stable in air at room temperature but decomposes on heating to 115°C or over[210].

Bis-(π-allyl)palladium and bis-(π-methylallyl)palladium are obtained by the reaction of anhydrous palladium chloride with allyl- and methylallyl-magnesium chloride respectively in ethereal solution at −40°C.[73,74,129]

Bis-(π-allyl)palladium is a yellow crystalline substance, m.p. 31°C, readily soluble in organic solvents, and does not react with alcohol or water. When hydrogen chloride is passed into an ethereal solution of bis-(π-allyl)palladium (−80°C) π-allylpalladium chloride is formed quantitatively. The latter is also formed by reaction of bis-(π-allyl)palladium with palladium(II) chloride[129].

B. Chemical Properties

a. Reactions leading to breaking of the halogen bridges. On treatment with cyclopentadienylsodium, bis-(π-allylpalladium chloride) gave a diamagnetic substance $(C_5H_5)(C_3H_5)Pd$ which was stable in air for a long time at low temperature[10,211]. The chemical properties of the product were studied in detail by Nesmeyanov and coworkers[212]. Reactions of π-allyl-π-cyclopentadienylpalladium with many electrophilic and nucleophilic reagents in acid, neutral, or alkaline media led to rapid removal of the cyclopentadienyl ligand. In the presence of an alkali metal halide the main product of the reaction was the bis-(π-allylpalladium halide). NaC_5H_5 reacts in an analogous fashion with the dimeric alkoxy-π-allylpalladium chlorides[36,185] and with complexes with cyclic allyl ligands[37,146-148,150,157,190].

$[(C_3H_5)(C_5H_5)Pd]$, just like $[(C_5H_5)(C_6H_9)Pd]$, on reacting with isopropyl or cyclohexyl isocyanide forms $[Pd(^iPrNC)_2]$ and $[Pd(C_6H_{11}NC)_2]$ respectively[213]. The reaction of $[(C_5H_5)(C_6H_9)Pd]$ with $AsCl_3$ or $SbCl_3$ proceeds by the reaction:

$$2\,C_5H_5PdC_6H_9 + AsCl_3 \rightarrow (C_6H_9PdCl)_2 + 2\,C_5H_5AsCl_2$$

with the formation of bis-(π-cyclohexenylpalladium chloride)[213].

A characteristic reaction of the π-allyl complexes with chlorine bridges is the breaking of the bridge by amines[36,37,187], which results in the formation of complexes of general formula [(allyl)PdCl(amine)]. Usually these compounds lose the amine easily, giving the initial complexes. Cryoscopic measurements have shown the monomeric structure of the compounds with the amines.

The infrared spectra of the products of addition of pyridine to $[(C_3H_5)PdCl]_2$ and $[(C_6H_{11})PdCl]_2$ had bands at 517 and 520 cm^{-1} respectively, owing to the retention of the π-allyl grouping in them[181]. With increase in the basicity of the amine there is an increase in the tendency of the complexes to decompose with separation of metallic palladium.

Moiseev and coworkers[181] consider that this decomposition is the result of the alkylation of the amine by the allyl grouping connected to the palladium atom:

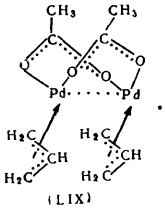
$$\pi\text{-}C_3H_5PdClNR_3 \rightarrow Pd + Cl^- + \overset{+}{N}R_3\text{—}C_3H_5.$$

However, it is possible that alkylation precedes the isomerisation of the complex, in which the π-allyl group is converted into a σ-bound ligand. A similar π–σ change of an allyl ligand is observed in the reaction of π-allyl complexes with triphenylphosphine[23-26] and dimethyl sulphoxide[25-27,175]. It was shown[24-26] that this change precedes the formation of an intermediate compound in which one π- and one σ-bond is present.

The Pd–Cl bond is covalent in all the monomeric complexes described in this section.

Compounds with an ionic Pd–Cl bond were obtained in using bidentate amines such as ethylenediamine and 2,2-bipyridyl (bipy)[214]. When bis-(π-allylpalladium chloride) or bis-(π-crotylpalladium chloride) reacts with these amines, taken in twofold molar excess, complexes are formed which are readily soluble in methanol and water. When the stoichiometric amount of 2,2′-bipyridyl is taken, a compound of the type $[(C_3H_5)Pdbipy]^+[(C_3H_5)PdCl_2]^-$ is obtained, in which a π-allyl ligand is present in both the cation and the anion. The preparation of other salts with the $[(C_3H_5)PdCl_2]^-$ anion has been described[215].

b. Replacement of the halogeno-bridges. Replacement of the chlorine bridges in π-allyl complexes of palladium by bromo- or thiocyanato-groups takes place readily on treatment with the corresponding alkali metal salt in a polar solvent (acetone, alcohol, etc.)[8,36,37,187,200]. Complexes with bridging carboxylato-groups (acetato-, propionato-, benzoato-, and trimethylacetato-) were made by treating acetone solutions of dichlorobis-(π-allylpalladium) complexes with the corresponding silver salt[46,187,216]. Cryoscopic and ebullioscopic measurements in benzene showed that all the complexes are dimers. They are somewhat less stable than the corresponding chloro-complexes. X-Ray diffraction examination of bis-(π-allylpalladium acetate) showed[46] that it has the structure (LIX) with a weak bond between the palladium atoms. Carboxylato-bridges are easily replaced by other groups. For example, on treating the acetato-complex with dry HCl, dichlorobis-(π-allylpalladium) was obtained, and treatment with trifluoroacetic acid gave the trifluoroacetato-complex $[(C_3H_5)(O_2CCF_3)Pd]_2$.



(LIX)

With acetylacetone and sodium carbonate, monomeric π-allylpalladium acetylacetonates are formed, which were obtained earlier on treating π-allylpalladium chlorides with thallium acetylacetonate[36,187] and also with sodium acetylacetonate. The π-allylpalladium acetylacetonates thus obtained have sharp melting points and can be used for the identification of the π-allyl complexes. Furthermore, it has been shown[217] that the hydrogen of the acetylacetonato-ligand is capable of being replaced by bromine under the action of *N*-bromosuccinimide. The action of other electrophilic and nucleophilic agents leads to loss of the acetylacetonato-ligand.

c. Reactions leading to breaking of the bond between the palladium and the allyl ligand. When heated to 145°C, $[(\pi\text{-}C_3H_5)PdCl]_2$ decomposes violently, the main products being allyl chloride and metallic palladium[8,172]. The decomposition of bis-(3-ethyl-1-methyl-π-allylpalladium chloride)[181]:

$$(C_6H_{11}PdCl)_2 \rightarrow 2\,C_6H_{11}Cl + 2\,Pd$$

and of some other complexes[172] took place in a similar fashion. However, when complexes with four or more carbon atoms in the allyl ligand are heated without solvent in a high vacuum, conjugated dienes are obtained[218].

As Christ and Hüttel showed[219], the reaction of π-allylpalladium chloride complexes with methanol solutions of potassium hydroxide leads to the formation of metallic palladium and an alkene with the same number of carbon atoms as in the π-allyl ligand. Reduction of the complexes $[(C_3H_5)PdCl]_2$ and $[(C_6H_{11})PdCl]_2$ with a methanol solution of sodium methoxide gave propene and hexene respectively[181].

Smutny[220] studied the decomposition products of methoxy-substituted π-allylpalladium chlorides on boiling in alcoholic medium with sodium acetate or hydrogen at room temperature.

During the bromination of $[(\pi\text{-}C_3H_5)PdCl]_2$ and other π-allyl palladium complexes there is stepwise absorption of two bromine molecules at each allyl–PdCl grouping[181,221]. In the first stage there is oxidation of the π-allylpalladium chloride with the formation of an acido-complex of the palladium and allyl bromide. In the second, slower stage, bromination of the C_3H_5Br takes place, which uses up another molecule of bromine.

Prolonged boiling of $[(\pi\text{-}C_3H_5)PdCl]_2$ with water in the presence of oxygen leads to the formation of propene and acrolein[172]. The oxidation of bis-(σ-methylallylpalladium chloride) goes only as far as α-methylacrolein[172,177]. A little isobutyraldehyde is apparently formed by the reaction

$$(C_4H_7PdCl)_2 + 2\,H_2O \rightarrow 2\,CH_3\text{—}CH(CH_3)\text{—}CHO + 2\,Pd + 2\,HCl.$$

π-Allyl complexes with substituted allyl ligands are oxidised in acid solutions in the presence of palladium(II) chloride, chromic acid, or manganese dioxide, to give the $\alpha\beta$-unsaturated carbonyl compounds[177]. The polarographic reduction of π-allylpalladium halides has also been studied[222].

The carbonylation of $[(\pi\text{-}C_3H_5)PdCl]_2$, just like that of the analogous nickel complex, leads to the formation of but-3-enoyl chloride as the main product, when the reaction takes place in benzene. In methanol solutions, there is direct conversion of the chloride into methyl vinylacetate[223]. Similarly, methyl 2-methylbut-1-enoate and methyl pent-2-enoate were obtained from the π-methylallyl and π-crotyl complexes[224].

The carbonylation of complex (LII) in benzene solution together with dichlorobutene gives 1-chloropent-2-enoyl chloride, from which in methanol and ethanol the corresponding esters of these acids are obtained[225,226].

On reaction with carbon monoxide in methanol, the π-allyl complex with a methoxycarbonyl group at a terminal carbon atom of the organic ligand (LV; R′ = CH_3, R = H) gives dimethyl pent-2-endioate.

From all the above examples it is clear that the attack of carbon monoxide proceeds at the terminal, less substituted carbon atom of the π-allyl group of the complex. There is also a report of the carbonylation of π-allyl complexes (LIV)[227].

Two interesting reactions were described recently, which also involve breaking the bond between the palladium and the allyl ligand. The reaction of $[(C_3H_5)PdCl]_2$ with $Fe_2(CO)_9$ leads, as a result of the transfer of the allyl ligand from the palladium to the iron, ($\pi \rightarrow \pi$ transfer), to the formation of tricarbonyl-π-allyliron chloride[228]:

$$(C_3H_5PdCl)_2 + Fe_2(CO)_9 \rightarrow 2\,C_3H_5Fe(CO)_3Cl + 2\,Pd + 3\,CO.$$

Treatment of bis-(π-allylpalladium chloride) with metallic mercury gives the quantitative yield of allylmercury(II) chloride ($\pi \rightarrow \sigma$ transfer)[229]. This method was used by the authors for the synthesis of a series of substituted allylmercury halides. In this reaction, as in the reaction with carbon monoxide, the attack of the mercury atom takes place at the unsubstituted terminal carbon atom of the π-allyl group.

Tsuji and coworkers[230,231] showed that the reaction of π-allylpalladium chloride with nucleophilic reagents (ethyl malonate, ethyl acetate, etc.) also leads to the splitting of the π-allyl complex:

$$(C_3H_5PdCl)_2 + 2\,X\overline{C}H{-}COOC_2H_5 \rightarrow 2\,CH_2{=}CH{-}CH_2{-}CHX{-}COOC_2H_5 + Pd + PdCl_2$$

where X = $CO_2C_2H_5$ or $COCH_3$.

The decomposition of ethyl diazoacetate in the presence of the π-allylpalladium chloride dimer has been described by Armstrong[232].

10. PLATINUM COMPLEXES

There is little information about π-allyl complexes of platinum. Bis-(π-allyl)platinum was obtained by the reaction of platinum(II) chloride with allylmagnesium chloride in ether at 0°C.[73,74,129] It is a colourless crystalline compound, m.p. 41°C, with a very unpleasant odour. Treatment of $[(C_3H_5)_2Pt]$ in pentane with hydrogen chloride at −80°C leads to the formation of $[(C_3H_5)PtCl]_2$, the structure of which has been shown by its reaction with NaC_5H_5.[129] This gives the complex $[(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Pt]$ prepared earlier[148] by the reaction of propeneplatinum chloride with a mixture of allylmagnesium chloride and cyclopentadienylsodium. The compound is lemon-yellow and stable in air.

Another π-allyl complex of platinum was described[30] recently. $[(C_3H_5)PtCl\{P(C_6H_5)_3\}_2]$, obtained as follows:

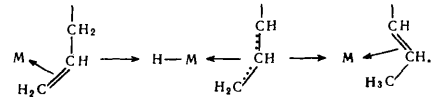
$$[(C_6H_5)_3P]_4Pt + C_3H_5Cl \rightarrow C_3H_5Pt[P(C_6H_5)_3]_2Cl + 2\,(C_6H_5)_3P.$$

IV. π-ALLYL COMPLEXES IN ORGANIC SYNTHESES

In this section we will discuss the participation of π-allyl complexes of the transition metals as intermediates in the isomerisation, oxidation, hydrogenation, carbonylation, and polymerisation reactions of unsaturated compounds.

1. ISOMERISATION OF ALKENES

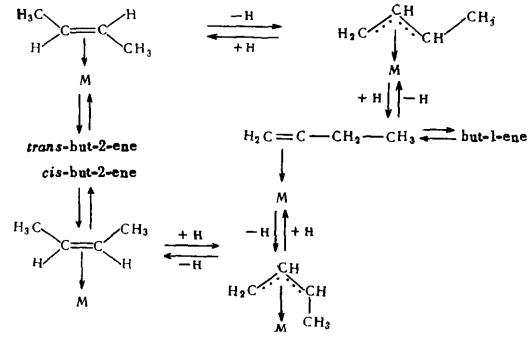
When treated with iron carbonyls[233,234], or with hydrogen carbonylferrate[235,236] or carbonylcobaltate[237], alk-1-enes isomerise into alkenes with non-terminal double bonds. A possible mechanism was proposed for these reactions, isomerisation with participation of the intermediate π-allyl metal hydride complexes[233,234,238,239]:



A similar scheme was proposed for the isomerisation of octenes[240] and of cyclo-octa-1,3-diene by iridium, palladium, and platinum compounds[241-244] and also of allyl alcohol to propionaldehyde by $Fe(CO)_5$.[85]

The isomerisation of alkenes by palladium salts evidently takes place analogously, with the formation of intermediate π-allyl complexes[245-247].

From the standpoint of the π-allyl mechanism Rooney and Webb[248] have explained the *cis–trans*-isomerisation of the monoalkenes. The general picture of the isomerisation of alkenes with the participation of π-allyl intermediate complexes can be represented as follows, for the example of the butenes:



The geometrical configuration of the alkene formed is determined by the structure of the intermediate π-allyl complex. The *syn*-isomer leads to *trans*-but-2-ene, and the *anti*-isomer gives *cis*-but-2-ene.

It is necessary to note that Davies[249], Harrod and Chalk[250], and Cramer and Lindsey[251] criticise the generality of the above scheme. For example, Cramer and Lindsey consider that the formation of π-allyl structures should lead sometimes even to inhibition of the isomerisation.

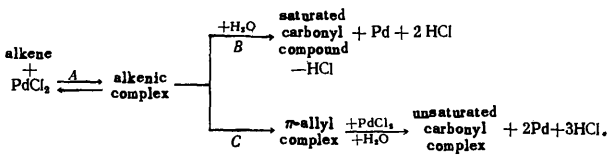
Asinger and coworkers[252] have proposed a method by which it is possible in some instances to confirm the π-allyl mechanism of the isomerisation of alkenes. When the isomerisation is carried out in a mixture with an alkene labelled with tritium, they think that the transfer of tritium will indicate the intermolecular hydride mechanism, but the absence of transfer, the intramolecular π-allyl mechanism.

2. OXIDATION OF ALKENES

In studying the catalytic conversion of alkenes into compounds of the platinum group metals, Smidt and coworkers[253] showed that methylglyoxal is formed from allyl halides.

Hüttel and coworkers [172] obtained the same product in the oxidation of bis-(π-allylpalladium chloride). In support of the π-allyl mechanism there is the identity of the products obtained in oxidising most alkenes and the corresponding π-allyl complexes listed in the Table (p. 488).

Hüttel and Christ [177] proposed the following general scheme for these reactions:



Depending on whether saturated or unsaturated carbonyl compounds are formed this scheme gives an answer about the nature of the intermediate complexes. The course of the reaction in direction *B* or *C* is determined mainly by the nature of the initial alkene, and primarily by its degree of branching. For example, linear aliphatic alk-1-enes give only saturated ketones [253] but branched alkenes listed in the Table give unsaturated carbonyl compounds [177].

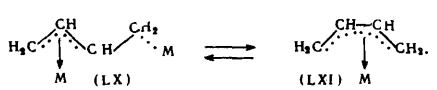
In the oxidation of the higher alk-1-enes by palladium chloride in anhydrous acetic acid containing sodium or potassium acetate, in the first stage π-allyl complexes are formed, which, as Vargaftik and coworkers have shown [254], are in equilibrium with the σ-allyl complex, the reaction of which with acetate ion give substituted allyl acetates:

$$R{-}CH{=}CH{-}CH_2PdCl + CH_3COO^- \rightarrow R{-}CH{=}CH{-}CH_2OCOCH_3 + Pd + Cl^-.$$

3. HYDROGENATION OF ALKENE DERIVATIVES

Kwiatek and coworkers who used the pentacyanocobaltate anion in aqueous solution to hydrogenate a series of organic compounds [255], later showed [107] that the intermediate products in these syntheses were cyano(allyl)cobalt complexes: whether they were π- or σ-complexes was mainly determined by the cyano:cobalt ratio. When butadiene was hydrogenated with a catalyst of low CN:Co ratio, *trans*-but-2-ene was mainly formed, but at high ratios but-1-ene was obtained. The authors explain these results by the formation of an intermediate cyano(methylallyl)cobaltate, in which at high CN:Co ratio the allyl ligand is connected to the cobalt atom by a σ-bond, and at low ratios by a π-allyl bond. The corresponding butene was obtained from these complexes on their reaction with the hydride $[CoH(CN)_5]^{3-}$.

The hydrogenation of buta-1,3-diene by transition metal compounds can, in the general example, pass through intermediate complexes of two types [248]:



On addition of hydrogen to these, the *syn*- and *anti*-forms of methyl-π-allyl complexes will be formed, which, in accordance with the above scheme, for the isomerisation of alkenes will give all three isomeric butenes.

4. CARBONYLATION OF ALLYL HALIDES

The carbonylation of allyl halides in the presence of nickel carbonyl was first described by Chiusoli [256-258]. On carrying out the reaction in water or alcoholic medium the corresponding acids or their esters were isolated:

$$R{-}CH{=}CH{-}CH_2Cl + CO + R'OH \xrightarrow{Ni(CO)_4} R{-}CH{=}CH{-}CH_2{-}COOR' + HCl.$$

The main product obtained from allyl chloride was vinylacetic acid, that from crotyl chloride, pent-3-enoic acid, etc.

In later work, Chiusoli and coworkers [259-262] showed the possibility of π-allyl complexes, $(\pi\text{-}C_3H_5)NiX(CO)$ where X = halogen, participating in these reactions as intermediates.

The carbonylation of allyl halides in the presence of acetylene is a reaction important for the synthesis of organic substances [127,258-267]. Here the π-allyl complexes formed as a result of the reaction of $Ni(CO)_4$ with the allyl halides then react with carbon monoxide in the presence of acetylene, with a molecule of acetylene being introduced between the allyl residue and the carbon monoxide. Hexa-2,5-dienoyl chloride is isolated under carbon monoxide pressure. In aqueous medium, in addition to hexa-2,5-dienoic acid a little phenol was obtained which shows that cyclisation takes place [263].

When the carbonylation of allyl halides is carried out in the presence of substituted acetylenes in water–acetone solution, cyclisation predominated with the formation of carboxyl derivatives of cyclopentenone and cyclohexenone [268,269].

Some of their derivatives behave similarly to the allyl halides in the carbonylation. Thus 1-chloro-4-cyanobut-2-ene gives 5-cyanopent-3-enoic acid, from which caprolactam can be obtained by hydrogenation, or caprylic acid in the presence of acetylene [258]. In the presence of acetylene 1,8-dichloro-octa-2,6-diene gave tetradeca-2,5,9,12-tetraen-1,14-dioic acid.

Prop-2-ynyl chloride also undergoes carbonylation in the presence of $Ni(CO)_4$ and water [270]. The main products are buta-2,3-dienoic and itaconic acids.

The identity of the products obtained from allyl chloride or allyl alcohol [271] and from bis-(π-allylpalladium chloride) [223] also supports the π-allyl mechanism of the carbonylation of allyl compounds with palladium catalysts ($PdCl_2$) at elevated temperatures. At room temperature allyl chloride gives 3,4-dichlorobut-3-enoyl chloride, and not but-3-enoyl chloride.

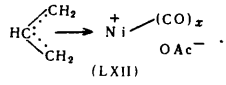
It has been shown that [272,273] that bis-(π-allylpalladium chloride) is an active catalyst for the carbonylation of allyl halides, giving alkenoyl chlorides as the main products, in high yields.

Of the other catalysts for the carbonylation of allyl derivatives, mention may be made of rhodium compounds [271] and platinum compounds [274].

5. SOME OTHER REACTIONS IN WHICH π-ALLYL INTERMEDIATE COMPLEXES PARTICIPATE

$\alpha\beta$-Unsaturated aldehydes and ketones are obtained in the hydroformylation of conjugated and non-conjugated

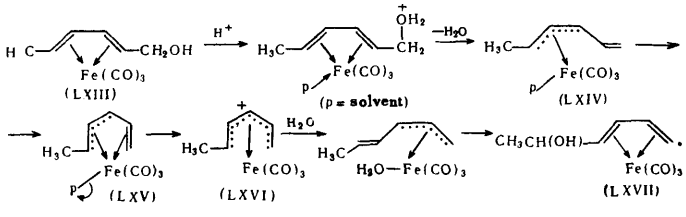
alkadienes in the presence of hydrogen tetracarbonylcobaltate(-1). Under the conditions of the reaction these aldehydes and ketones are easily reduced by the hydrogen tetracarbonylcobaltate(-1) through an intermediate π-oxapropenyl complex of type (XXIV) to saturated aldehydes and ketones[80]. The same complex evidently participates in the reaction for the formation of 1,2-dibenzoyloxystilbene from benzoyl chloride or bromide and tetracarbonylnickel in tetrahydrofuran or hexane solution[275]. As Bauld has shown[276], the reaction of allyl acetate with $Ni(CO)_4$ proceeds through the stage of complex (LXII), the structure of which is analogous to that of complex (XXXIX), and leads to biallyl:



(LXII)

Bicinnamyl is obtained in the same way from cinnamyl acetate.

Mahler and coworkers[277,278] showed that some of the reactions of tricarbonyldieniron complexes can be satisfactorily explained by starting from the formation of π-allyl complexes. For example, the action of strong acids on tricarbonyl(hexa-*trans*-2,*trans*-4-dien-1-ol)iron (LXIII) gives the intermediate π-allyl complexes (LXIV, LXV) and then tricarbonyl-*syn*-1-methylpentadienyliron cation (LXVI)[274], which on hydrolysis is converted into tricarbonyl(hexa-*trans*-3,5-dien-2-ol)iron (LXVII)[275]:

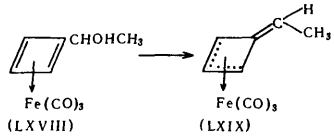


(LXIII) (LXIV) (LXV) (LXVI) (LXVII)

Pettit and coworkers[279] proposed a π-allyl structure (LXIX) for the intermediate product formed on treating complex (LXVIII) with hydrochloric acid followed by solvolysis in methanol.

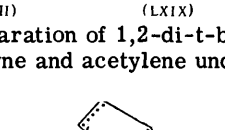
$Co_2(CO)_4[C_2H{-}C(CH_3)_3]_2(C_2H_2)$ (LXX).

Mills and Robinson[280] used X-ray structural analysis and NMR spectroscopy to show the π-allyl nature of the intermediate product:



(LXVIII) (LXIX)

obtained in the preparation of 1,2-di-t-butylbenzene from 3,3-dimethylbut-1-yne and acetylene under the influence of cobalt carbonyl:



(LXX)

6. POLYMERISATION AND OLIGOMERISATION OF ALKENES AND ALKADIENES

Catalysts based on π-allyl complexes of nickel have been studied in most detail.

Wilke found that bis-(π-allyl)nickel brings about the cyclic trimerisation of butadiene into cyclododeca-1,5,9-triene[23,125,127]. Bis-(π-methylallyl)nickel and bis-(π-crotyl)nickel behave in the same manner[129,281].

π-Allylnickel halides initiate the stereospecific polymerisation of butadiene[130,282-285]. The microstructure of the polymer formed is determined by the nature of the halogen in the π-allyl complex: compounds which contain chlorine lead to *cis*-1,4-polymers, whereas iodine complexes are capable of forming polybuta-1,4-dienes. It has been shown radiochemically that the π-allylnickel ligands of the initial complexes entered into the composition of the polymer[286].

The products of the reaction of π-allylnickel halides with Lewis acids (halides of B, Al, Ti, Sn, V, Mo, and W) exhibit high activity in the polymerisation of butadiene[130,282,283,285,287]. In this, irrespective of the halogen in the π-allyl complex or in the Lewis acid, polybutadienes with a high proportion of *cis*-1,4-links are formed[283].

Active catalysts for the polymerisation of butadiene are also formed in the reaction of bis-(π-crotyl)nickel with the halides of various metals[130,281,282,287]. The proportion of links of different configurations in the polymers obtained under the influence of these systems is determined by the nature of the halogen in the metal halide[281,282].

The products of the reaction of π-cyclopentadienyl(π-cyclopentyl)nickel with Lewis acids act similarly[288,289].

Propene and ethylene are dimerised extremely rapidly in the presence of catalytic systems consisting of bis-(π-allyl)nickel or bis-(π-allylnickel halides), aluminium halides or alkylaluminium halides, and trialkylphosphines[23,29,290,291]. It has been shown[23,29] that the basicity of trialkylphosphines affects the structure of the dimers formed.

Bis-(π-allylnickel bromide) polymerises cyclobutene with opening of the double bond: a polycyclobutylenamer is formed[284]. There is also a report of the polymerisation of acetylene in the presence of bis-(π-allylnickel bromide)[138,139]. Crystalline 1,2-polyallene was obtained in the presence of $Ni(\pi\text{-}C_3H_5)_2$, $[NiBr(\pi\text{-}C_3H_5)]_2$, and $[Ni(\pi\text{-}CH_2CHCN)_2]$[292].

Bis-(π-allyl)cobalt iodide polymerises butadiene to *cis*-1,4-polymer[23,29,128,290].

The π-allyl cobalt complex of composition $CoC_{12}H_{19}$ described by Natta and coworkers[124] is a catalyst for the linear dimerisation of butadiene and 3-methylhepta-1,4,6-triene. The same dimer is also formed by the action of tris-(π-allyl)cobalt[23,29,290,293].

1,2-Polybutadiene is formed in the presence of tris-(π-allyl)chromium[23,29,63,128,281,290]. The products of the reaction of $(\pi\text{-}C_3H_5)Cr$ with $NiCl_2$ or TiI_4 bring about the formation of *cis*-polybuta-1,4-diene, but with $NiBr_2$ the *trans*-1,4-polymer is obtained[281].

Bis-(π-allyl)chromium iodide, like bis-(π-allyl)nickel, catalytically trimerises butadiene into cyclododeca-1,5,9-triene[23,29,63,128]. In the presence of $(\pi\text{-}C_3H_5)_2CrCl$ butadiene is converted into a polymer[63]. Furthermore, it must be mentioned that at room temperature and moderate pressure (15 atm) $(\pi\text{-}C_3H_5)_3Cr$ polymerises ethylene into linear high-molecular-weight polyethylene, analogous to the polyethylene obtained with Ziegler catalysts[63].

Bis-(π-allyl)palladium converts butadiene solely into linear oligomers, whereas its addition products with electron donors gives cyclic dimers[23,129].

Tris-(π-allyl)iron gives a mixture of cyclic and aliphatic oligomers, and also polymerises but-2-yne into hexamethylbenzene[101].

An examination of the mechanism of the polymerisation of diene hydrocarbons with participation of π-allyl complexes allowed ideas of primary importance to be formulated about the formation of the links of a polymeric chain as a function of the direction of attack of the active centre of the monomer molecule[283,294-296]. The polymerisation of butadiene in an aqueous medium under the influence of the rhodium compounds has been examined from the aspect of a π-allyl mechanism[297-299].

---oOo---

Several new papers on the subject of the present review have appeared whilst the latter was being written.

The reaction of π-allylpalladium chlorides with electron donors has been investigated by NMR and infrared spectra[300-302]. Hegarty and Kitching[303] have interpreted the ultraviolet spectra of π-allyl complexes of palladium in various solvents. Several papers[304-307] have described the preparation of π-allyl complexes of palladium. Moiseev and coworkers[308] investigated the thermal decomposition of six π-allyl complexes of palladium.

Wilkinson and coworkers[309] prepared new allyl complexes of rhodium. The results of an X-ray diffraction study of bis-(π-allyl)rhodium chloride have been reported[310].

Nesmeyanov and coworkers[311] studied the decomposition products of carbonyl-π-allyl complexes of iron. King[312,313] has studied the π-allyl complexes of molybdenum and iron.

The participation of π-allyl complexes of the transition metals as intermediate products in isomerisations has been discussed[314-317]. A patent[318] deals with the polymerisation and copolymerisation of alkenes under the influence of the π-allyl complexes of Cr, Mo, W, and Zr.

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DEHYDROGENATION OF ALKANES AND ALKENES AT LOW PRESSURES

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I. INTRODUCTION

The catalytic dehydrogenation to alkenes and alkadienes of alkanes containing 2 to 5 carbon atoms is a promising method for the preparation of unsaturated hydrocarbons. In recent years there has been greatly increased interest in the preparation of alkenes and alkadienes by the catalytic dehydrogenation of low-molecular-weight alkanes at low pressures of the starting materials, because thermodynamic calculations have shown that under these conditions considerable yields of useful products should be obtained. Notwithstanding a certain complexity in the technological design of dehydrogenation processes at low hydrocarbon pressures (that is, under vacuum or with the use of solvents), the application of such processes results in substantial economic gains. It is for this reason that, in the United States and Western Europe, the production of bivinyl by Houdry's method has been developed as the most economic method of dehydrogenation[2]; in this method n-butane is dehydrogenated under vacuum in a single stage[1]. In the USSR the problem of using this method is under consideration[3,4].

A large amount of experimental information on the catalytic dehydrogenation of hydrocarbons at low pressures is now available, and this merits a special review; in our opinion such a review provides an essential supplement to modern informative reviews[5-7] on the dehydrogenation of hydrocarbons. The present review considers problems of the thermodynamics of the dehydrogenation of C_2–C_6 hydrocarbons at low pressures, as well as catalysts and the operating conditions for industrial applications of the process.

II. THERMODYNAMIC CALCULATIONS OF HYDROCARBON DEHYDROGENATIONS

Thermodynamic calculations permit us to select the optimal conditions for carrying out a reaction. Using such calculations, we can calculate whether a given reaction could proceed in such a way as to give a useful product in sufficiently high yield to warrant its practical application, and also the most favourable temperatures and pressures for carrying out the reaction. An increase in the temperature of a process and reduction in pressure result in an increase in the degree of equilibrium dehydrogenation, and therefore favour an increased yield of alkenes or alkadienes[5,8].

Using experimental data on the dehydrogenation of alkanes in the presence of chromium catalysts, Frey and Huppke[9] determined the equilibrium constants for the dehydrogenation of n-butane to each of the isomeric butenes, and of propane to propene, and ethane to ethylene. Using the data of these workers, Zharkova[10] determined the dependence of $\lg k_{equil}$ on temperature. Dement'eva and coworkers[11,12] calculated the dependence of the degree of dehydrogenation of n-butane, isobutane, and propane on

temperature and pressure. Moreover, using experimental results on the dehydrogenation of n-butenes to buta-1,3-diene on chromium(III) oxide at 404–534°C, these workers also calculated the equilibrium constants of this reaction for the temperature range mentioned. Kassel[13] and Pitzer[14] calculated the equilibrium constants for the dehydrogenation of butane and the equilibrium composition at various temperatures. Aston and coworkers[15] calculated equilibrium constants for the dehydrogenation of n-butane to n-butene and buta-1,3-diene at 25–1227°C, and of individual n-butenes and their mixture to buta-1,3-diene over the same temperature range. The difference between the values of k_{equil} found experimentally[9] and the calculated values[15] is due to experimental errors in the investigation of a mixture with components present in low concentrations.

Balandin and coworkers[16] made a thermodynamic calculation of equilibria in the butene–butadiene system, and found that the yields of butadiene increase with decreasing pressure, the most favourable results being obtained at a temperature of 550–600°C and a pressure below atmospheric.

Using published data[6,17], Bogdanov[18] derived an equation for determining the equilibrium composition in the dehydrogenation of n-butane to n-butenes and buta-1,3-diene in the presence of an inert gas or water vapour as diluent. The author regards the dehydrogenation of n-butane as consisting of two successive reactions: n-butane is first dehydrogenated to n-butene (a mixture of isomers of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene), and the butenes are then dehydrogenated to buta-1,3-diene. For this reason, the equilibrium constants for these reaction were calculated for each isomer separately, and the values found were then used to calculate the overall equilibrium constant (Table 1).

The values of the constants obtained are in satisfactory agreement with the corresponding values obtained by other workers. Dilution of n-butane with an inert gas greatly improves conversion into n-butenes and buta-1,3-diene. At 527°C and with a 1 : 5 molar dilution of butane with inert gas, the conversion of butane into butenes and butadiene reaches 62.5%, compared with 36.7% without dilution. At 527°C and a 1 : 10 dilution with inert gas the conversion of n-butenes to buta-1,3-diene is 28.7%, compared with 10% without dilution[18]. Dilution of a butane–butene mixture (30% of n-butenes and 70% butane) with an inert gas also increases the degree of conversion into butadiene. Thus, at 600°C and a 1 : 5 dilution, conversion increases from 13.8% without dilution to 34.3%, that is, by a factor of two and a half. The authors point out that dilution with hydrogen leads to a sharp fall in conversion.

TABLE 1. Temperature dependence of the equilibrium constants for the dehydrogenation of n-butane to n-butenes (total isomers) and of n-butenes to buta-1,3-diene[18].

Temperature, °C	k_{equil} (dehydrogenation of n-butane to n-butenes)	k_{equil} (dehydrogenation of n-butenes to buta-1,3-diene)
427	0.0111	0.000680
527	0.154	0.0102
627	1.21	0.0851
727	6.35	0.462

In a thesis, Khodakov[19] derived an equation for calculating the equilibrium conversion of n-butane into butenes (mixture of isomers) and an equation for the calculation of the equilibrium conversion of n-butane with allowance for side-reactions, that is, when the process is not selective.

As with C_4 hydrocarbons, in the dehydrogenation of isopentane, a reduction in pressure and an increase in temperature also increases the yield of isoprene.

Ghosh and Roy[20] studied the reaction equilibrium in the dehydrogenation of 3-methylbut-1-ene at 330–450°C and a pressure of 10–35 mmHg on an aluminochromium catalyst with the addition of oxides of vanadium and molybdenum. These workers determined the equilibrium constants at the temperatures mentioned and calculated the dependence of free energy change on temperature for the dehydrogenation of isopentane to methylbutene, and of methylbutenes to isoprene. Shuikin and coworkers[21,22] calculated the equilibrium constants and the degree of dehydrogenation for the conversion of isopentane into methylbutenes at 327–627°C and atmospheric pressure. Bogdanov and Bol'shakov[23,24] made a detailed thermodynmaic calculation for the dehydrogenation of isopentane, methylbutenes, and isopentane–methylbutene mixtures at 427–727°C. The equilibrium constants and compositions of the equilibrium mixtures were calculated over the given temperature range at atmospheric pressure and at inert gas dilutions of 1 : 1 to 1 : 10 (molar). Calculations analogous to those used for the dehydrogenation of butane, butenes, and their mixtures were used to determine the overall equilibrium constant k' for the dehydrogenation of isopentane to methylbutenes (mixture of isomers); this constant was taken as the sum of the equilibrium constants of the dehydrogenation of isopentane to 2-methylbut-1-ene (k_1'), 3-methylbut-1-ene (k_2'), and 2-methylbut-2-ene (k_3'):

$$k' = k_1' + k_2' + k_3'.$$

The overall equilibrium constant for the dehydrogenation of methylbutenes to isoprene, k'', is calculated from the equation:

$$\frac{1}{k''} = \frac{1}{k_1''} + \frac{1}{k_2''} + \frac{1}{k_3''},$$

where k_1'', k_2'', and k_3'' are the equilibrium constants for the dehydrogenation to isoprene of 2-methylbut-1-ene, 3-methylbut-1-ene, and 2-methylbut-2-ene respectively. The calculated equilibrium constants were used to determine the composition of the equilibrium mixtures formed in the dehydrogenation of isopentane to methylbutenes and isoprene. The degree of conversion of isopentane into methylbutenes and isoprene was calculated from the composition of the equilibrium mixtures (Table 2).

The figures in Table 2 clearly show that dilution of isopentane with an inert diluent at atmospheric pressure, or a corresponding reduction of total pressure in the system, greatly increases the conversion of isopentane into methylbutenes and isoprene. Thus, at 527°C and a molar dilution of 1 : 5 the conversion into methylbutenes and isoprene reaches 80.8%, compared with 57.8% without dilution. Temperature change greatly influences the nature of the isopentane conversion. At temperatures below 600°C isopentane is converted mainly into methylbutenes, but at higher temperatures the conversion of isopentane into isoprene increases sharply, and smaller amounts of the methylbutenes are formed. At very high temperatures, particularly at very low pressures, isoprene is the main dehydrogenation product.

TABLE 2. Effect of an inert diluent on the conversion of isopentane into methylbutenes and isoprene at various temperatures.

Temperature, °C	Dilution of isopentane, molar ratio	Conversion of isopentane, % into methylbutenes	into isoprene	into methylbutenes + isoprene	Temperature, °C	Dilution of isopentane, molar ratio	Conversion of isopentane, % into methylbutenes	into isoprene	into methylbutenes + isoprene
427	1:0	19.1	0.1	19.2	627	1:0	74.8	15.0	89.8
	1:5	37.9	0.7	38.6		1:5	61.9	35.3	97.2
	1:10	47.1	1.0	48.1		1:10	52.5	46.3	98.8
527	1:0	55.9	1.9	57.8	727	1:0	50.9	47.4	98.3
	1:5	73.3	7.5	80.8		1:5	28.4	71.3	99.7
	1:10	75.0	11.9	86.9		1:10	20.1	79.6	99.7

Fridshtein and Chechik[25] made a thermodynamic calculation for the isopentane–methylbutenes–isoprene–hydrogen system over the temperature range 450–650°C for pressures of 1, 0.3, and 0.2 ata. These workers determined the equilibrium constants for the dehydrogenation of isopentane and isopentane–methylbutene mixtures to isoprene, and also the equilibrium composition of the dehydrogenation products (Fig. 1). These calculations showed that a significant yield of isoprene and methylbutenes can only be obtained at a temperature higher than 550°C and a pressure lower that 0.3 ata.

It follows from calculations of the equilibrium composition of mixtures in the dehydrogenation of methylbutenes (mixture of isomers) and isopentane–methylbutene mixtures to isoprene[23] that a reduction of pressure in the system, or dilution of the starting material, significantly increases the degree of conversion into isoprene (Fig. 2).

The work of Chang and coworkers[26] is also of interest; they established the relationship between the individual methylpentenes formed when isopentane is dehydrogenated under vacuum, and they give the equilibrium constants and equilibrium composition of the reaction products at 427–627°C at a residual pressure of 100 mmHg and also at atmospheric pressure (Fig. 3). Reduction of the pressure increases the yield of isoprene; thus at 602°C and 100 mmHg it is thermodynamically possible almost completely to decompose isopentane to yield 51.7% of methylpentenes and 46.5% of isoprene. These results are in good agreement with calculations made by other workers[23–25].

With C_6 hydrocarbons, a thermodynamic calculation for the dehydrogenation reaction has only been made for one isomer—neohexane[27].

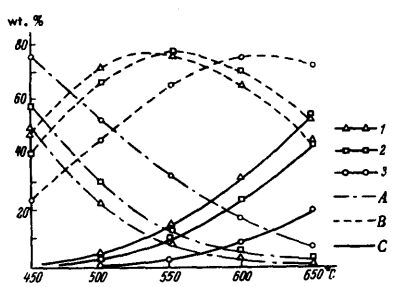


Fig. 1. Equilibrium composition of products of dehydrogenation of isopentane at different pressures: 1) 0.2 ata, 2) 0.3 ata, 3) 1.0 ata; *A*) isopentane; *B*) methylbutenes; *C*) isoprene.

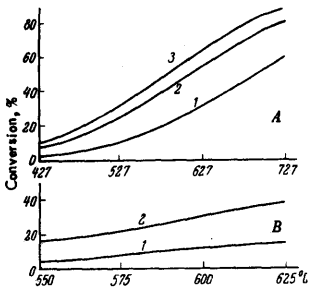


Fig. 2. Effect of an inert diluent on the conversion of methylbutenes into isoprene (*A*) and isopentane–methylbutene mixtures (70 : 30) into isoprene (*B*) as a function of temperature: 1) without dilution; 2) dilution 1 : 5; 3) dilution 1 : 10.

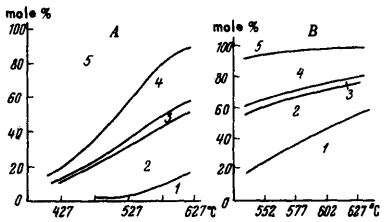


Fig. 3. Equilibrium composition of dehydrogenation products of isopentane at atmospheric pressure (*A*) and at a residual pressure of 100 mmHg (*B*): 1) isoprene; 2) 2-methylbut-2-ene; 3) 3-methylbut-1-ene; 4) 2-methylbut-1-ene; 5) isopentane.

Thus the thermodynamic data show convincingly that the most suitable conditions for the dehydrogenation of alkanes and alkenes to give alkadienes are high temperatures (~600–700°C) and low pressures (~100 mmHg).

Thermodynamic calculations do not, of course, give any indications of reaction rates, but only indicate the most suitable conditions for the reaction. It is therefore necessary to find catalysts which increase the rate of a given reaction and suppress side-reactions which reduce the yield of required products.

It is also useful to examine the behaviour of petroleum hydrocarbon fractions at high temperatures and low pressures in the absence of catalysts. It has been shown in a number of papers on the thermal cracking and pyrolysis of alkanes under reduced pressure that at 400–800°C the hydrocarbons are cleaved at the C–C bonds[28–48]. Dehydrogenation takes place to only a slight extent.

At high temperatures, ethane[28–35] and ethylene[36] give a number of saturated and unsaturated C_1–C_4 products.

When propane is subjected to a cracking process at 590°C and a pressure of 20 mmHg, it is decomposed to a slight extent (up to 10%) and the sum of the $H_2 + C_3H_6$ products formed is equal to the sum of the $CH_4 + C_2H_4$ products[37]. When the degree of decomposition increases, the predominating reaction is demethanisation, that is, the amount of $CH_4 + C_2H_4$ formed is greater than the amount of $H_2 + C_3H_6$ produced.

TABLE 3. Composition of issuing gas in the thermal cracking of isopentane (820°C, 109 mmHg, $\tau_{contact}$ = 0.015 s).

Composition of gas	Content, %	Composition of gas	Content, %
iso-C_5H_{12}	19.0	C_3H_6	12.4
α-C_4H_8	0.7	C_3H_8	0.4
β-C_4H_8	6.0	C_2H_2	0.2
iso-C_4H_8	5.6	$C_2H_4+C_2H_6$	16.0
C_4H_6	0.4	CH_4	23.1
n-C_4H_{10}	0.4	H_2	17.0
iso-C_4H_{10}	0.1	coke(CO_2)	0.2

The main reaction that occurs in the cracking of butane[40] is decomposition into methane and propene, and to a lesser degree into ethane and ethylene. Dehydrogenation proceeds to only a slight extent[40-42]. Reports on the kinetics and mechanism of thermal decomposition of butane have been published[43,44]. Isobutane[40] decomposes preferentially into 2-methylpropene and hydrogen (580°C, 20 mmHg), smaller proportions decomposing into methane and propene, and into ethane and ethylene.

When the cracking of propane is initiated by the addition of 1–3% of azomethane, dehydrogenation predominates over demethanisation[45]. The reverse is true for isobutane[45]. In the sensitised cracking of butane, the direction of the reaction and the ratio of the products are the same as in ordinary cracking.

Isopentane is cracked[46-48] preferentially into C_2 and C_3 hydrocarbons; butenes are formed to a lesser extent (Table 3).

The thermal decomposition of hydrocarbons is a free-radical chain reaction. The predominant decomposition of the hydrocarbon molecules at the C–C bond in contrast to decomposition at the C–H bond (dehydrogenation) under thermal-cracking conditions is due to the lower energy of the C–C bond compared with the C–H bond[49]. Catalysts can change the direction of the thermal decomposition reaction so that dehydrogenation of alkanes and alkenes to alkadienes becomes the predominant reaction.

III. CATALYSTS FOR THE DEHYDROGENATION OF ALKANES AND ALKENES AT LOW PRESSURES

The extensive patent literature that has appeared over the past 25 to 30 years is evidence of the great amount of work that has been done in the selection and study of catalysts for the dehydrogenation of alkanes and alkenes to alkadienes at low pressures. More than 100 patents giving proposed catalysts for these processes have been published during this period, mainly in the United States, but also in England, France, the Federal German Republic, and other countries. Most of the catalysts refer to the preparation of butadiene and isoprene from the corresponding alkenes; the minority have been proposed for producing these diene hydrocarbons from the alkanes n-butane and isopentane. Reduction of pressure is achieved either by dilution with water vapour or an inert gas or by evacuation. The composition of the catalysts varies with the method used to reduce the pressure.

Several types of catalysts have been developed for the dehydrogenation of mono-alkenes diluted by water vapour. The ones that have been used most extensively are those proposed by the firm Standard Oil Development, based on oxides of metals of Group II of the Periodic System: Mg [50-60], Zn [61,62], Be [61-64]; their composition includes iron(III) oxide, and also copper(II) oxide as a stabiliser and potassium oxide as a promoter. The general composition of catalysts of this type may be expressed as follows (parts by weight): $MO:Fe_2O_3:CuO:K_2O = 80:20:5:5$, where M = Mg, Zn, or Be. Of such catalysts, Catalyst 1707 has been used industrially; it has the following composition (wt.%): 72.4 MgO; 18.4 Fe_2O_3; 4.6 CuO; 4.6 K_2O.[51-57] Various modifications of these catalysts were examined in the course of their development[50,51,55,61,65-67]. CaO and SrO [50,51,56] have been proposed as promoters, and oxides of Ag, Zn, Cd, Th, Co, and Mn [51] as stabilisers. Iron(III) oxide has been replaced by MnO_2.[61]

The Shell Development Company and others have done work on the selection of catalysts based on iron(III) oxide with potassium compounds as promoters[68-77] and also with the inclusion of oxides of Cr, Bi, Ti, Al, and compounds of Cu, Pb, and Li. The catalysts of this type that have been most widely used are Contact Shell 105 (9 Fe_2O_3, 4 Cr_2O_3, 6 K_2CO_3) and Contact Shell 205 (Contact Shell 105, but with a higher content of K_2CO_3).[1]

For the dehydrogenation of butenes to butadiene, the firm I. G. Farbenindustrie used a catalyst consisting of more than 50% of ZnO and oxides or salts of Cr, V, Mo, U, W, etc.[78-81]; zinc oxide has also been used with other additives[82].

Schulze and coworkers (Phillips Petroleum Company)[83-85] patented a bauxite catalyst for this process; this consists of bauxite and the oxide or hydroxide of Ba, Mg, Sr, or Cr; they also patented catalysts containing combinations of Al_2O_3 with oxides or hydroxides of Ba, Mg, and K [86]. Bauxite catalysts have also been tried in processes in which the starting material is diluted with inert gases[87-89].

Britton and Dietzler (Dow Chemical Company) and other workers (Esso Research Company) have made a new type of catalyst (nickel phosphate catalyst) for the dehydrogenation of alkenes in the presence of water vapour[90-95]. A similar catalyst has been developed in Czechoslovakia[96,97]. Its composition may be represented by the formula $Ca_8Ni(PO_4)_6$. The addition of small amounts of Cr_2O_3 and graphite improves the properties of this catalyst[90,92-95].

There are references[98] to the use of graphite and carbon as catalysts; these have been tried for n-butenes diluted with water vapour, N_2, and CO_2. Silver vanadate[99] and metals of Group VIII (Ni) [100] have been used as catalysts in this process with CO_2 as the diluent, and CaO has been used with N_2 as the diluent[101], but these catalysts have not found extensive use.

All the catalysts described have been tried in the dehydrogenation of n-butenes to butadiene under various conditions (550–800°C, space velocity 100–800 h^{-1}), the alkenes being diluted with water vapour in the ratio 1:7 to 1:15. The use of a CaNi–phosphate catalyst requires the introduction of large quantities of water vapour (the ratio of n-butenes to water vapour is 1:20). The operating life without regeneration of Type 1707 and CaNi–phosphate catalysts is 0.5–1 h; catalysts based on Fe_2O_3 can be

used without regeneration for 8–12 h, and bauxite catalysts for 6 h. Regeneration is effected by means of superheated steam, alone or mixed with air. On Catalyst 1707 the yield of butadiene calculated on the butenes passed through is 28 to 30%, and the selectivity is 68 to 85%; the catalyst is stable and does not lose its activity or selectivity over a period of several months. Iron and bauxite catalysts give a lower conversion of n-butenes into butadiene (20–26% and 20% respectively).

On a CaNi–phosphate catalyst butenes are converted into butadiene in 30–35% yield; under production conditions this catalyst gives a butene conversion of 35% with a selectivity of 86–88%. Thus, the use of a CaNi–phosphate catalyst ensures high yields of butadiene, based on butenes passed through and decomposed, although it requires regeneration more frequently and is more expensive than catalysts based on iron oxide. The useful life of a CaNi–phosphate catalyst is 6–7 months, and that of an iron catalyst 2–3 months.

All the types of catalysts encountered in patents for use in the dehydrogenation of n-butenes in the presence of water vapour have also been used for the dehydrogenation of methylbutenes to isoprene: this includes Type 1707 catalyst[59], iron[77], zinc[82], bauxite[83], and CaNi–phosphate catalysts[90,94,97]. The best yields of isoprene (over 40%) were obtained with a CaNi–phosphate catalyst over the temperature range 640–650°C, with a space velocity of 0.9–1.0 h^{-1}, a 1 : 17 dilution with water vapour, and a contact time of 5–10 min[97]. 2,3-Dimethylbutane was dehydrogenated to 2,8-dimethylbutadiene on the same catalyst[94].

The catalytic dehydrogenation of alkanes to unsaturated hydrocarbons in the presence of water vapour has not been widely used: the available information consists of isolated references[102,103] indicating that n-butane is converted into a mixture of butenes and butadiene in 20% yield on an aluminochromium catalyst containing V_2O_5 or MoO_3.

In the dehydrogenation of alkanes, alkenes, and their C_4–C_5 mixtures under reduced pressure, aluminochromium catalysts[104–118] containing about 20% of Cr_2O_3, sometimes with the addition of 1–5% of BeO, SiO_2, and K_2O, are mainly used[96,119–121]. These catalysts are notable for their high activity, long-term stability, and the simplicity with which they are prepared. Thus, in the dehydrogenation on an aluminochromium catalyst (80% Al_2O_3, 20% Cr_2O_3)[113] of a butane–butene mixture containing 62% of butenes, the yield of butadiene is 18–21% (590–600°C, 50 mmHg, contact time 0.2 s). A chromium–vanadium oxide catalyst[122] has also been used for the dehydrogenation of butane–butene mixtures. In the dehydrogenation of monoalkanes under reduced pressure, apart from aluminochromium catalysts, catalysts consisting of Al_2O_3 in a mixture with V_2O_5 and Ag[123], or oxides of Ti, Zr, Ce, Hf, Th[124] and V, Ce, Ta[125], have been used. When the first of these catalysts[123] is used, butenes are converted into butadiene in 35% yield (660°C, 97 mmHg, 482 h^{-1}).

In some instances, the partial pressure of the starting hydrocarbon was reduced by dilution with hydrogen[126,127].

Several papers on the dehydrogenation of hydrocarbons under the conditions mentioned above deal with catalysts of practical interest, but do not propose any fundamentally new catalysts.

Thus, the search for active and selective catalysts for use in the dehydrogenation of alkanes and alkenes at low pressures, which has long been in progress, is still being intensively pursued at the present time.

IV. DEHYDROGENATION OF BUTANE AND BUTENES TO BUTADIENE

The dehydrogenation of butane, butenes, and their mixtures to buta-1,3-diene at low pressures of the initial hydrocarbons has been studied at fairly high temperatures. In addition to the main dehydrogenations, in which butane is converted into a mixture of butene isomers, and the butenes to butadiene, the process is accompanied by a number of side-reactions, such as isomerisation, formation of saturated and unsaturated C_1–C_3 hydrocarbons, as well as coke formation on the catalyst, which necessitates its regeneration. These reactions are undesirable since they lower the yield of the required product, buta-1,3-diene. The extent to which they occur depends on many factors, including the composition of the catalyst, the degree of hydrocarbon conversion, and the conditions under which the process is carried out.

Fedorov and coworkers[128] studied the dehydrogenation of but-2-ene diluted with nitrogen on different catalysts. On the best of these, magnesium oxide, the yield of butadiene was 25–29%.

Balandin and coworkers[16,129–131] studied the dehydrogenation of butenes to butadiene on chromium catalysts at low pressure, the starting material being diluted with nitrogen and carbon dioxide. When a 1 : 7.5 dilution with carbon monoxide was used at 600°C the yield of butadiene was 34.2 with a selectivity of 75%. It was found that the following side-reactions occurred, in which carbon dioxide reacted with butene and with hydrogen:

$$C_4H_8 + 4\,CO_2 = 8\,CO + 4\,H_2,$$
$$H_2 + CO_2 = H_2O + CO.$$

The side-reactions play only a small part here, since the yield of butadiene increases with increasing dilution. Experiments in which butenes were dehydrogenated on a chromium catalyst at a residual pressure of 180 mmHg showed that, when the temperature is increased from 550° to 600°C, the yield of butadiene increases from 14 to 28–29%, that is, by a factor of two[16]. In addition to the dehydrogenation of butene[131], reactions occur in which the initial butene and the butadiene formed are decomposed and hydrogenated. But-1-ene and but-2-ene are dehydrogenated at about the same rate[130]. Experiments with a mixture of butene and butadiene show that the decomposition of butadiene increases with temperature and also with its concentration in the initial mixture.

Grosse and coworkers[132] dehydrogenated n-butenes on an aluminochromium catalyst at 600°C and 190 mmHg. Under these conditions a lower yield of butadiene per pass was obtained (18–23%).

Balandin and coworkers[131] studied the kinetics of dehydrogenation of butene on a chromium catalyst at low pressure. The kinetic equation has the following form:

$$V = k\,\frac{[C_4H_8]}{[C_4H_8] + \Sigma Z_n [A_n]},$$

where k is the dehydrogenation rate constant; Z_n is the relative adsorption coefficient of a compound; and A_n is its partial pressure.

The apparent activation energy of butenes and bivinyl at a residual pressure of 180 mmHg with a contact time of 0.3 s was 26.3–27.9 kcal $mole^{-1}$ at 551–660°C, and 34.3–34.7 kcal $mole^{-1}$ at 535–559°C.

This reaction has also been studied by Shcheglova and Pshezhetskii[133] at 450–500°C and butene partial pressures of 0.05–0.3 atm, nitrogen being used as a diluent; they found that the kinetics of dehydrogenation of n-butenes on an aluminochromium catalyst correspond to the equation:

$$W = kC_2^{0.5}$$

where C_2 is the concentration of butene.

The value found for the activation energy was 27 ± 1 kcal mole^{-1}. They showed that the addition of 10% of hydrogen has no effect on the rate of dehydrogenation of butene, but 20% of hydrogen slightly reduces the rate. The addition of butadiene did not significantly reduce the rate of dehydrogenation. However, the relative adsorption coefficients of butene, butadiene, and hydrogen on an aluminochromium catalyst indicate that butadiene has a high adsorption coefficient, that is, on a catalytically active surface butadiene is more strongly adsorbed than butene, but hydrogen is adsorbed to about the same degree as butene; the adsorption coefficients of butene, butadiene, and hydrogen at 560°C are in the ratios 1 : 9.5 : 0.82.[131] Thus the presence of butadiene must have an appreciable effect on the rate of dehydrogenation.

When butadiene is dehydrogenated on a mixed oxide catalyst[134] in the presence of water vapour the ratio of the relative adsorption coefficients for butene, butadiene, and hydrogen is found to be 1 : 4.9 : 0.8 at 580°C, and 1 : 3.7 : 0.8 at 600°C.

Beakberger and Watson[135] found that, with Catalyst 1707, and water vapour as a diluent, the rate of the reaction may be expressed by the following equation:

$$W = \frac{k\left(P_{C_4H_8} - \frac{P_{C_4H_6} \cdot P_{H_2}}{k_{equil}}\right)}{(1 + k_{C_4H_8} \cdot P_{C_4H_8} + k_{C_4H_6} \cdot P_{C_4H_6} + k_{H_2} \cdot P_{H_2} + k_A P_A)^2}$$

where k is the rate constant; k_{equil} is the equilibrium constant of the dehydrogenation reaction; $k_{C_4H_8}$, $k_{C_4H_6}$, k_{H_2}, k_A are the equilibrium adsorption constants for C_4H_8, C_4H_6, H_2, and aromatic compounds respectively; and P is the partial pressure. The activation energy of this process, with water vapour as the diluent, was 17 kcal mole^{-1}.

For the same n-butene dehydrogenation on an oxide-type industrial catalyst with water vapour as diluent, Tyuryaev and Kolobikhin[136] give another kinetic reaction of the form: $r = kP^n_{C_4H_8}$, where $P_{C_4H_8}$ is the partial pressure of the butenes, and $n = 0.35$ (found by a graphical procedure).

The mechanism of dehydrogenation of butane and butene has also been studied by means of radioactive carbon, ^{14}C.[137,138] A mixture (1 : 1) of butane and butene, diluted with water vapour (1 : 9) was dehydrogenated on a chromium catalyst at 635°C. The results of the experiment show that the formation of butadiene is mainly due to the dehydrogenation of butene:

$$C_4H_{10} \rightarrow C_4H_8 \rightarrow C_4H_6.$$

It was then shown[137] that, in addition to dehydrogenation, a reaction occurs in which hydrogen is exchanged between butane and butene, that is, hydrogenation of butene and dehydrogenation of butane occur at the same time. The rates of dehydrogenation of butane to butene (W_1), to butadiene (W_2), and of butene to batadiene (W_3) on a chromium catalyst are related by the following ratios: $W_1 : W_2 : W_3 = 20 : 1 : 1000$.

$$C_4H_{10} \xrightarrow{W_1} C_4H_8 \xrightarrow[W_3]{} C_4H_6$$

Thus butadiene is formed from butene, and there is virtually no conversion of butane into butadiene.

When the reaction is carried out on an aluminochromium catalyst at a pressure of 250 mmHg and a temperature of 600°C, that is, under conditions favouring the dehydrogenation of butane[138], more than 96% of the butadiene formed is derived from butene. The ratio of the reaction rates then is: $W_1 : W_2 : W_3 = 18 : 1 : 25$.

The ratio $W_1 : W_2$ is therefore the same for dehydrogenation on a chromium as on an aluminochromium catalyst. Carbon and resinous products are formed by the decomposition of butene and, to a greater extent, of butadiene[138,139]. If the process is carried out in the presence of water vapour, a large amount of carbon dioxide is formed, and no coke is deposited since the greater part of the carbon deposited on the catalyst is oxidised to CO and CO_2 by the water-gas reaction. The reaction rates for the formation of CO_2 from C_4H_6, C_4H_8, and C_4H_{10} are in the ratio 60 : 4 : 1 [137]; this shows that the formation of CO_2 is the result of a secondary bivinyl-conversion reaction. Kolobikhin and Tyuryaev[140] studied the reaction for the conversion of butadiene in the presence of water vapour on a catalyst used for the dehydrogenation of n-butenes. They showed that the main reactions are the hydrogenation of butadiene and its decomposition to give coke. The greater part of the coke reacts with water vapour to form CO and CO_2. Coke deposition appears to be the main cause of the reduction of catalyst activity.

Beakberger and Watson[135] and Kearby[141] carried out experiments on the dehydrogenation of n-butenes on Catalyst 1707 and its modifications, water vapour being used as diluent. In addition to butadiene and hydrogen, the dehydrogenation products also contained low-molecular alkenes and alkanes (propene, ethylene, propane, ethane, methane) and carbon dioxide. At 665°C, with butenes at a space velocity of 500 h^{-1} and a water-vapour dilution of 1 : 14, the yield of butadiene is 28%, based on the amount of butene passed through, and 74% based on the amount decomposed. Results of the industrial use of Catalyst 1707 and of catalysts based on iron oxide (Shell-105 and Shell-205) are also given in articles by Reidel[142], Reilly[143], and Kearby[5]. Britton and Dietzler[144] obtained better yields of butadiene on a catalyst of composition $Ca_8Ni(PO_4)_6$ containing 1–2% of chromium(III) oxide. When a high water-vapour dilution was used (molar ratio of water vapour to butene 20 : 1) on a laboratory apparatus, the yield of butadiene was 93–97% based on n-butenes consumed, the conversion being 20–45% (525–650°C, space velocity 100–200 h^{-1}). Increasing the duration of the cycle from 1 to 2 h reduces the conversion of n-butene by 2–3%. The conversion increases as the space velocity decreases.

Thus, on this catalyst the dehydrogenation is characterised by high yields and selectivity. However, a disadvantage is the high yield of carbonyl compounds (4% of the butene obtained) and acetylene hydrocarbons (1%) [143].

Data on the industrial use of calcium–nickel–phosphate, termed Dow B, are given in papers by several authors[143,145,146]. At 620–680°C, a butene space velocity of 125–175 h^{-1}, and a molar ratio of water vapour to n-butene of 20 : 1, butadiene was obtained in 90–94% yield with a conversion per pass of 45–55%.[146]

Diaconescu and coworkers[147] dehydrogenated butenes on a catalyst consisting of a mixture of oxides of magnesium, iron, copper, and potassium (73.5; 18.0; 4.3; 4.2% respectively) and a catalyst based on calcium and nickel

phosphates (PO_4 58.0; Ca 33.3; Ni 6.6; Cr_2O_3 2.17). The best yields of butadiene were obtained on a calcium–nickel–phosphate catalyst.

Recently great attention has been paid in the Soviet Union to the single-stage dehydrogenation of n-butane to butadiene. Single stage dehydrogenation greatly simplifies the technological arrangement as compared with the two-stage process, since it is no longer necessary to separate the butenes from the products of the first dehydrogenation stage. Moreover, the large amount of water vapour used in the dehydrogenation of the butenes to butadiene is saved. The single-stage method is advantageously carried out by dehydrogenatiny butane–butene mixtures, since fresh butane is sent for dehydrogenation with the recirculating butane–butene mixture that remains after separation of the butadiene from the reaction products. A large number of patents, but only a small number of papers, have been published on the direct preparation of butadiene from n-butene. A method for the preparation of bivinyl in one stage was first studied by Pshezhetskii and coworkers[148]. A butane–butene mixture containing 32–38% of butenes was dehydrogenated on an aluminochromium catalyst. At a temperature of 600°C and a pressure of 100–150 mmHg, the yield of butadiene was 14–15%, based on the amount of mixture passed through, and 60–68% based on the amount consumed. Dehydrogenation of pure n-butane under the same conditions gave 10.9 to 12.4% of butadiene based on the amount of butane passed through.

Balandin and coworkers[149] obtained 31% of butadiene, based on the amount of butenes passed through, or 15.7% based on the amount of butane–butene mixture (57 : 43) passed through at 600°C, 180 mmHg, and a contact time of 0.82 s.

Komarewsky[150] dehydrogenated butane on a selective dehydrogenation catalyst at 540–650°C and pressures of from 35 to 753 mmHg. The conversion to butadiene was 12.2% of butane per pass, with only slight carbon deposition (0.2%). By recirculation, 74% of butadiene can be obtained with only 2.3% of coke being deposited on the catalyst. Dehydrogenation of a technical butane–butene fraction of cracking gas (containing 35.7% of butenes) on a chromium catalyst at 180 mmHg and 600°C gave a butadiene yield of 31–35.5% based on the amount of butene passed through, or 9–10% based on the total flow[151].

Bogdanova and coworkers dehydrogenated butane–butene mixtures on an oxide catalyst in the presence of water vapour[152]. When the butene content of the initial mixture is increased from 41.4 to 65%, the yield of butadiene based on the total flow increases from 16.9 to 24.1%, but the yield based on the amount of butene passed through decreases from 40.8 to 38.4%. The yield of butadiene based on butene passed through increases in comparison with the yields obtained in experiments with pure butene because butane acts as a diluent, lowering the partial pressure of the butenes. On this catalyst butane is dehydrogenated only to a slight extent.

The catalysts K-3 and K-5 were found to be insufficiently active and selective in the dehydrogenation of a butane–butene mixture (60 : 40) at 600°C [18] (molar dilution with nitrogen 1 : 4 to 1 : 5). Under these conditions the yield of butadiene was 15–17% based on mixture passed through, and 70–75% based on mixture consumed. In the presence of hydrogen, a significantly lower amount of butadiene was obtained per pass. At the same time the yield of butadiene based on the amount of raw material decomposed increases because the thermal decomposition of butadiene, which is accompanied by the elimination of hydrogen, is inhibited. Worse results were obtained when methane, ethylene, or propene was used as a diluent. In experiments on the dehydrogenation of butane–butene mixtures containing 33% of butene at 600°C and 140 mmHg, 19% of butadiene was obtained[153]. Blowing the catalyst with hydrogen at high temperature improves the characteristics of the process (the yield of butadiene increases, the catalyst becomes more selective, and less coke is deposited). This is due to desorption at high temperature of the water formed when the catalyst is reduced by hydrogen.

Lyubarskii and coworkers[154] studied the kinetics of dehydrogenation of n-butane on an aluminochromium catalyst containing 6% of chromium(III) oxide at 460–500°C and partial butane pressures of from 0.1 to 1 atm, with nitrogen as diluent[154]. It was found that the reaction is inhibited by butene; a small amount of butene in the starting gas greatly reduces the degree of conversion of butane. Admixture of hydrogen has little effect on the rate of dehydrogenation. The kinetics of dehydrogenation are represented by the equation:

$$W = k_1 \frac{C_1}{C_2^{0.5}}$$

where C_1 is the concentration of butane, and C_2 is the concentration of butenes.

The effective rate of dehydrogenation of butane with allowance for reversibility of the reaction is expressed by the following equation[7]:

$$W_{\text{eff}} = k_1 \frac{C_1}{C_2^{0.5}} - k_2 C_2^{0.5} C_{H_2},$$

where C_{H_2} is the concentration of hydrogen.

The activation energy for the dehydrogenation of n-butane to butenes with nitrogen as diluent was 40 ± 1 kcal mole^{-1} at 460–500°C.

The conditions have been established[153] for the single-stage dehydrogenation of butane on Catalyst K-117; these are: a temperature of 590°C, a pressure of 150 mmHg, an operating cycle of 7 min, a space velocity of 400–600 h^{-1}, and a 67 : 33 butane–butene mixture.

On the industrial scale, the single-stage dehydrogenation of butane to butadiene has been effected by Houdry's method. The results of operations on the first semi-industrial and industrial plants for the dehydrogenation of butane and butane–butene mixtures have been described[155,156]. Butane was dehydrogenated on chromium(III) oxide–aluminium oxide catalysts at 580–590°C, at a residual pressure of 130 mmHg and a space velocity of 1–1.5 h^{-1}. The total duration of the cycle is 20 to 25 min, with a contact time of 7–10 min. The yield of butadiene is 32.7% based on the butane passed through. Later, the single-stage process was perfected and adopted industrially in the United States[157,158], the German Federal Republic[159], and France[160]. Dehydrogenation is carried out under vacuum on an aluminochromium catalyst. The duration of the dehydrogenation and regeneration cycles is 7–10 min. The amount of heat adsorbed in the endothermic dehydrogenation is balanced by the heat evolved in the burning of the coke deposited on the catalyst during regeneration. To ensure thermal balancing in the process, the catalyst is mixed with an inert material with a high heat

capacity, such as alundum, kaolin, refractory brick, etc. Fresh butane being fed into the dehydrogenation process is first mixed with the recirculating butane–butene mixture obtained after the butadiene has been removed from the dehydrogenation products of the initial mixture. The following are the optimal parameters for the process and the yield of butadiene reported in the literature[158]: temperature 600–607°C, pressure 100–150 mmHg, space velocity 2 h^{-1}, yield of butadiene 50–55%.

Bol'shakov has reviewed the literature on the single-stage dehydrogenation of butane to butadiene in reactors with an adiabatic regenerative cycle[161].

V. DEHYDROGENATION OF ISOPENTANE AND PENTENES

In the catalytic dehydrogenation of isopentane, three alkene isomers with the iso-structure are formed: 3-methylbut-1-ene, 2-methylbut-1-ene, and 2-methylbut-2-ene, and these are converted into isoprene. Table 4 gives data on the dehydrogenation of individual pentenes, with both the normal and iso-structure, and their mixtures.

Both Grosse and coworkers[132], and Mamedaliev and coworkers[162], concluded that the degree of dehydrogenation of methylbutenes is independent of the position of the double bond. On cannot agree with Grosse's conclusion, since the dehydrogenation of individual methylbutenes was studied with different contact times. Gorin and coworkers[163] established that 3-methylbut-1-ene is dehydrogenated to a lesser degree than two other methylbutenes under the same conditions. This conclusion has been confirmed by the work of Bogdanova and coworkers[164], in which higher yields of isoprene were obtained in the dehydrogenation of 2-methylbut-2-ene. Having studied the isomerisation of methylbutenes under dehydrogenation conditions, these workers suggested[164] that isoprene is mainly formed from 2-methylbut-2-ene, and to a lesser extent from 2-methylbut-1-ene, but 3-methylbut-1-ene isomerises to the two other methylbutenes. They studied the dehydrogenation of individual methylbutenes to isoprene with water vapour as a diluent and showed that the activation energies for the dehydrogenation of all three isomers are similar (20.9–22.1 kcal $mole^{-1}$).

TABLE 4. Data on the dehydrogenation of individual pentenes and their mixtures.

Starting alkene	Catalyst	Pressure (mmHg) or water vapour dilution	Temperature, °C	Space velocity (h^{-1}) or contact time, s	Yield of alkadiene, wt. % of raw material	Reference
3-Methylbut-1-ene	Cr—Al c with 4% Cr_2O_3	190	600	0.05 s	21.4	132
2-Methylbut-2-ene + + 2-methylbut-1-ene	ditto	190	600	0.39 s	22.3	
Pent-2-ene	»	190	600	0.40 s	30.3	
3-Methylbut-1-ene	K-16	180	600	2.0 h^{-1}	28.5	162
2-Methylbut-1-ene	»	180	600	2.0 »	26.0	
3-Methylbut-1-ene	K-16	1:10	540	2.0 »	22.7	163
2-Methylbut-1-ene	»	»	540	2.0 »	27.2	
2-Methylbut-2-ene	»	»	540	2.0 »	27.7	
Mixture of methylbutenes	»	»	540	2.0 »	26.5	
ditto	Cr—Al	190	600	860—2000 h^{-1}	35	148
»		1:2.3–3.3	600	5 h^{-1}	30.6	164—166
»	Cr—Al of firm "UOR"	80	630	2.95 h^{-1}	35.6	167
»	ditto	80	660	1.53 h^{-1}	47.5	
»	Al—Cr—K	1:7 (diluent: N_2)	625	10 h^{-1}	30	168
2-Methylbut-2-ene	1707	1:14	665	500 h^{-1}	35.5	141
Mixture of methylbutenes	CaNi—phosphate	1:15—20	635	85—400 h^{-1}	35.3	144
2-Methylbut-2-ene		1:2.5—3	560 and 620	4.5—5.5 h^{-1}	20.4 and 41.3	164
2-Methylbut-1-ene		»	ditto	ditto	17.5 and 39	
3-Methylbut-1-ene		»	»	»	15.5 and 31.8	
n-Pentenes	mixed oxide	1:2.6—3.5	540—640	3—8 h^{-1}	12.3—25.6	169

Balandin and coworkers have studied the dehydrogenation of methylbutenes in the presence of water vapour[165,166]. It was found that the greatest yields of isoprene were obtained when the methylbutenes were diluted with water vapour in the ratio 1 : (2.3–3.3) by weight. With lower dilution ratios the yield of isoprene decreases, and the amounts of light hydrocarbons and carbon dioxide formed increase. In addition to the main reaction in which the methylbutenes are dehydrogenated to isoprene, demethanisation also occurs with the formation of butene and butadiene; the methylbutenes are hydrogenated to isopentane and isoprene is decomposed with the formation of light hydrocarbons and carbon dioxide. At 600°C and a space velocity of 5 h^{-1}, in the presence of water vapour, the yield of isoprene is 30.6% of the methylbutenes passed through. The activation energy for the dehydrogenation of a mixture of methylbutenes to isoprene was 23.3 kcal $mole^{-1}$.[165]

Mamedaliev and coworkers[170] dehydrogenated a mixture of methylbutenes in a semi-technical apparatus with a 0.5 litre reactor using K-16 Catalyst at 540°C and a space velocity of 2 h^{-1}, with water vapour as a diluent in the ratio of 7–10 moles per mole of starting material; they obtained a catalysate containing 23% of isoprene. The yield of isoprene on the methylpentenes passed is not stated. Kearby[141] dehydrogenated 2-methylbut-2-ene at a somewhat higher temperature (665°C) in the presence of Catalyst 1707 and water vapour (in the ratio 1 : 14) as a diluent and obtained a high yield (35.5%) of isoprene with a selectivity of 71%. Britton and Dietzler obtained a similar yield on calcium–nickel–phosphate catalyst at 635°C, the starting hydrocarbons being diluted with water vapour[144].

The dehydrogenation of normal pentenes has been studied by Grosse and coworkers[132], by Guyer[123], and by Bogdanova and others[169].

A number of workers have carried out the dehydrogenation of isopentane. Bogdanova and coworkers[171] have shown that, on an oxide catalyst at 580–620°C, and with a space velocity of feed of 5.5 h^{-1} and a 1 : 3 dilution with water vapour, comparatively low yields (4–8%) of isoprene are obtained. Mamedaliev and coworkers[172,173] studied the dehydrogenation of an isopentane fraction on Catalyst K-5 at 600–615°C with hydrogen as diluent; they found that the best yields of dienes (8.2–8.8%), on the basis of isopentane passed through, are obtained when the isopentane is diluted 1 : (3–4) with hydrogen. Higher yields of isoprene have been obtained on a catalyst developed at the All-Union Research Institute for Synthetic Rubber (VNIISK)[174]. The process was carried out at a low partial pressure of isopentane, obtained by using nitrogen as a diluent. It was shown that an increase in temperature or an increase in the degree of dilution leads to an increased content of diene hydrocarbons in the catalysts. The yield of diene hydrocarbons at 575°C, a space velocity of 1.1 h^{-1}, and a 1 : 4 dilution with nitrogen is 14.5%. High yields of isoprene (26–28.5% based on isopentane passed through) were obtained by Kolupaeva and coworkers[175] in the dehydrogenation of isopentane on an aluminochromium catalyst, previously activated in a stream of hydrogen, at a temperature of 600°C, a pressure of 100 mmHg, and a space velocity

of 0.4 h^{-1}. They showed that when the pressure is reduced the proportion of isoprene in the reaction products is increased in comparison with the proportion of the isopentanes. The yield of normal C_5-hydrocarbons is less than 1%. The studies mentioned here were made in a flow system with a stationary catalyst layer.

Chang and coworkers[26] studied the kinetics of dehydrogenation of isopentane on aluminochromium oxide catalysts in a fluidised bed at 500–600°C and a pressure of 100–500 mmHg. Although the equilisation of concentrations in the fluidised bed leads to inhibition of the process and an increase in the proportion of side-reactions, fairly high yields of isoprene were obtained per pass: at 600°C, 100 mmHg, and a contact time of 2.2 s, the yield of isoprene was 15.8% based on the amount of isopentane passed through. These workers found that the observed activation energy of the dehydrogenation reaction was 44 kcal $mole^{-1}$. The kinetics of dehydrogenation of isopentane have also been studied by Shirokov[176], using an aluminochromium catalyst at 471–521°C and 0.2–1 atm. He found that the kinetics of the reaction could be represented by the following equation:

$$W = k\frac{C_1}{C_2^{0.4}},$$

where C_1 and C_2 are the concentrations of isopentane and methylbutenes at the reactor outlet. The activation energy of the process was 38 kcal $mole^{-1}$, a value differing only slightly from the more recent values given above[26].

Like butadiene, isoprene can be prepared from isopentane by two methods: single-stage and two-stage. In the two-stage method, isopentane is dehydrogenated to methylbutenes on one catalyst; the methylbutenes are then separated from the reaction products and dehydrogenated on another catalyst to isoprene. The isolation of the methylbutenes from the catalysate is a complex problem because of the closeness of the boiling points of the components and the difficulty of separating the azeotropic mixtures formed. Isoprene can be obtained in one stage by the dehydrogenation of isopentane–methylbutene mixtures. The process is carried out on a single catalyst and it is not necessary to separate the methylbutenes from the isopentane. The difficulty of the single-stage process lies in the selection of suitable catalysts and in finding the conditions under which the dehydrogenation of isopentane to methylbutenes proceeds simultaneously with the dehydrogenation of the methylbutenes to isoprene; the conversion of isopentane into methylbutenes must not be less than the conversion of methylbutenes into isoprene. Isoprene is separated from the catalysate obtained in the dehydrogenation of isopentane–methylbutenes mixtures, and isopentane is added. The quantity of isopentane is adjusted so that the conversion of isopentane exceeds the conversion of methylbutenes. The isopentane–methylbutenes mixture is again subjected to dehydrogenation. The extent to which the process is single-stage (φ) is determined[177] by the ratio of the concentration of methylbutenes in recycle (σ') to the concentration of methylbutenes in the initial isopentane–methylbutene mixture (σ):

$$\varphi = \frac{\sigma'}{\sigma} \times 100.$$

A value of φ necessary for operation of the single-stage process may be achieved at certain ratios of the process parameters. A number of workers have obtained the ratio of conversion of isopentane and methylbutenes needed for single-stage dehydrogenation (Table 5); isopentane is consumed in the formation of isoprene, but at the same time there is a slight increase in the amount of methylbutenes[174]. The results of Mavity and Zetterholm[167] and those of Fridshtein and coworkers[174] on the dehydrogenation of methylbutenes and mixtures of methylbutenes and isopentane show that the yields of isoprene increase with decreasing pressure, or increasing dilution with nitrogen, and also with increasing temperature, and when the isopentene content of the starting material is increased. But as the temperature is increased, or the content of methylbutenes in the mixture is reduced, the selectivity of the process is reduced, and more coke is formed[174,178]. Increasing the contact time beyond 0.6 s does not increase the yield of isoprene, because this also increases the rate of secondary reactions (dimerisation and decomposition of isoprene, and coke formation). Isopentane has been dehydrogenated in a single-stage by Houdry's method[179] on a semi-technical apparatus with recycling of the unreacted products. The mixture subjected to dehydrogenation contained 16.6% of methylbutenes; the yield of isoprene was 12.1 wt.% based on the amount of mixture passed through, and 51.8 wt.% based on the amount converted.

To determine the optimal conditions for the dehydrogenation of isopentane–methylbutenes mixtures when the process is operating in one stage, Bol'shakov[180] studied the effect of temperature, space velocity, pressure, and content of methylbutenes in the mixture on the main characteristics of the process on Catalyst K-N. Table 6 gives his results.

In the same paper, Bol'shakov reported that when the partial pressure of the hydrocarbons is reduced by dilution with an inert gas such as nitrogen, the main characteristics of the single-stage process are impaired in comparison with dehydrogenation under vacuum. Thus, when nitrogen was used as a diluent, the yield of isoprene was 15% based on the amount of mixture passed through, and 50% based on the amount of mixture converted, the process being 100% single stage; under similar conditions but with the application of reduced pressure, the yield of isoprene increased to 17.7% based on the amount passed through, and 65% based on the amount of mixture converted, the process being single stage to the extent of 116%.[180]

Gorin and coworkers made a somewhat different approach to the dehydrogenation of isopentane–methylbutene mixtures[163]. In order greatly to simplify the two-stage scheme for the preparation of isoprene from isopentane, these workers proposed that dehydrogenation conditions

TABLE 5. Dehydrogenation of isopentane–methylbutene mixtures under single-stage conditions (according to data from different authors).

Temperature, °C	Pressure (mmHg) or dilution with nitrogen (molar ratio)	Space velocity, h^{-1}	Conc. of methylbutenes in initial mixture, wt.%	Conc. of isoprene in catalysate, wt.%	Yield of isoprene, wt.%: on hydrocarbons passed	Yield of isoprene, wt.%: on hydrocarbons decomposed	Conc. of methylbutenes, wt.%: in catalysate after separation of isoprene	Conc. of methylbutenes, wt.%: in catalysate recycle	Degree of single-stage operation	Reference
630	80	606	15	13.4	12.8	74.1	19.4	16.0	107	167
575	1:3	450	30	17.5	15.7	60.6	40.2	30.1	100	177
575	1:4	1350–1100	25	—	14.5–14.0	67–70	—	—	single-stage conditions achieved	174
600	100	0.4 (liquid)	21.4	—	27	61.5	—	21.4	ditto	178

TABLE 6. Optimal conditions for single-stage dehydrogenation of isopentane to isoprene on Catalyst K-N.

Partial pressure, mmHg	190
Temperature, °C	575
Space velocity, h^{-1}	450
Content of methylbutenes in mixture, %	27—28

should be so chosen that the ratio of methylbutenes to isopentane in the catalysate after separation of isoprene would be the same as the ratio of these compounds in the initial mixture. After separation of the isoprene from the reaction mixture, the mixture obtained can be sent for dehydrogenation having been mixed with a fresh portion of isopentane–methylbutene mixture of the same composition obtained in the first stage of the dehydrogenation of isopentane. The experiments showed that, at 580°C and a pressure of 190 mmHg, dehydrogenation of n-butane and butene [sic. pentane and pentene? (Ed. of Translation)] on a catalyst gives a catalysate containing 15–18% of isoprene (Table 7). The ratio of the methylpentenes to the isopentane in the initial mixture is the same as that in the catalysate (40 : 60).

Bogdanova and coworkers [171] studied the dehydrogenation of a prepared mixture of isopentane and methylbutene ($C_5H_{10} : C_5H_{12} = 1 : 1$) and of a catalysate (ratio 1 : 1.3) obtained on an aluminochromium catalyst after the first stage of the dehydrogenation of isopentane. These workers consider that the best results are obtained at 600–620°C, with a space velocity for the mixture 5–6 h^{-1} and a 1 : 3 dilution with water vapour. Under these conditions, the yield of isoprene is 38–40% based on isopentenes passed through and 88–92% based on the amount of mixture reacting.

Satisfactory results have also been obtained in the dehydrogenation of isopentane–methylbutene mixtures (60 : 40) diluted with benzene in the molar ratio 1 : 3. [163] Isopentane–methylbutene mixtures (70 : 30) have also been diluted with nitrogen–hydrogen mixtures [174] containing 0 to 50% of hydrogen. In the presence of hydrogen, the concentration of unsaturated hydrocarbons changes little, but the concentration of alkadienes decreases, as does also the degree of coke formation. Thus, as might be expected, the presence of hydrogen in the starting mixture has an inhibitory effect on the formation of isoprene.

A very important characteristic of the isopentane dehydrogenation process is the amount of coke deposited on the catalyst, which is determined by the temperature and duration of the experiment [181]. The amount of coke deposited increases with the methylbutene content of the mixture, and the coke is removed by the hydrogen. Tyuryaev and Balashova have suggested the following mechanism for coke formation [181]: isoprene → cyclic dimer → ... (polycondensation, decomposition, dehydrogenation)... → polycyclic hydrocarbons.

TABLE 7.

Temperature, °C	Space velocity, h^{-1}	Yield of catalysate, wt. %	Content of isoprene in catalysate, wt. %	Yield of isoprene, wt. %		Ratio $C_5H_{12} : C_5H_{10}$ in catalysate
				on mixture passed through	on mixture decomposed	
580	6	92.6	18.4	17.2	70.0	61.3:38.7
580	8	95.6	15.0	14.3	77.1	60.5:39.5

VI. DEHYDROGENATION OF C_6-HYDROCARBONS

Alkadienes have been prepared from C_6-alkanes and mono-alkenes on catalysts used for the dehydrogenation of butane and butenes to butadiene, the hydrocarbon being diluted with water vapour, hydrogen, or nitrogen [27,182–184].

Nazarov and coworkers [182] found that, on Catalysts K-12, K-16, and K-18, which are used for the conversion of butenes to butadiene, at temperatures of 600–675°C, space velocities of 1000–2000 h^{-1}, and a 1 : 8 water-vapour dilution, 2,3-dimethylbut-2-ene is converted into 2,3-dimethylbuta-1,3-diene. The yield of alkadiene on Catalyst K-16 is 20–23% based on the quantity of alkene passed through, and 40–50% based on the amount that reacts. Under similar conditions [181], on this catalyst, 2-methylpent-3-ene gives 10–13% of diene hydrocarbons (isoprene and 2,3-dimethylbuta-1,3-diene), calculated on the amount of hydrocarbon passed through.

A group of workers [183,184] dehydrogenated 2,3-dimethylbutane and its mixtures with 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene (containing 54% of alkenes) on Catalyst K-5 at 630°C, a space velocity of 2 h^{-1}, and 1 : 4 hydrogen dilution. These workers pointed out that the yield of alkenes and alkadienes (12–14% of starting material) does not depend on the position of the double bond in 2,3-isomers present in the starting mixture. When a mixture of 2,3-dimethylbutane with 2,3-dimethylbutenes (40%) diluted 1 : 8 by volume with water vapour is dehydrogenated on Catalyst K-16, a yield of 12–12.2% of alkadienes is obtained [184]. Timofeeva and coworkers [185] studied the dehydrogenation of 2,2-methylbutane on an aluminochromopotassium catalyst at 500°C, a space velocity of 0.72 h^{-1} at atmospheric pressure, with helium as an inert diluent. Comparison of the results showed that dilution increases the yield of 3,3-dimethylbut-1-ene in comparison with dehydrogenation at atmospheric pressure from 8–9 to 10–12%. Other workers, who carried out the reaction in vacuum on an aluminochromium catalyst also obtained ~10 wt.% of alkene [186].

Thus, in the dehydrogenation of the C_6 hydrocarbons described above, because of side-reactions, fairly low yields of unsaturated dehydrogenated products are obtained, although higher yields are thermodynamically possible. It is well known that the equilibrium yield of dehydrogenation products increases with increasing molecular weight [5–7].

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Certain conclusions can be drawn from the literature survey on the conversions of alkanes and alkenes at low pressures.

It is thermodynamically more advantageous to dehydrogenate alkanes and alkenes for the purpose of obtaining alkadienes at temperatures above 600°C and very low pressures. However, because of technological difficulties and increased cracking at high temperatures, the process cannot be carried out under these conditions. It is therefore expedient to carry out the dehydrogenation at 550–600°C and a pressure of 100–200 mmHg. Low partial pressures are obtained by evacuation, or by the use of inert diluents.

The use of nitrogen, methane, or carbon dioxide as a diluent greatly increases the volume of the contact gas, and this makes the condensation and separation of the reaction products very complicated. Water vapour has a number of advantages compared with the diluents mentioned above: it can be easily separated from the reaction products, it also serves as a heat carrier, and since it reacts with coke deposited on the catalyst, no special regeneration of the catalyst is necessary. In the dehydrogenation of mono-alkenes and alkadienes in the presence of water vapour, the most active catalysts were found to be those based on oxides of magnesium, iron, zinc, and phosphates of calcium and nickel. Other catalysts, even those that are active dehydrogenation catalysts, for example, aluminochromium catalysts, are rapidly deactivated in the presence of water vapour. For this reason, dehydrogenations of alkane and alkene hydrocarbons and their mixtures on aluminochromium catalysts are carried out in the presence of inert diluents, such as nitrogen, or under vacuum. The use of low pressures produced by evacuation in the dehydrogenation process is more effective than dehydrogenation in the presence of diluents, although operation under vacuum requires that the plant should be hermetically sealed to prevent air being sucked in. Most of the catalysts described in the literature for the dehydrogenation of alkanes, alkenes, and their mixtures at low pressures are not sufficiently selective. Further development of these processes therefore requires that a search should be made for new and more effective catalysts.

Kinetic studies of the dehydrogenation processes considered here have permitted elucidation of the most probable mechanism for the reactions and, in a some instances, have made it possible to select the optimal conditions for the process. However, a number of kinetic studies have been made at an unsatisfactory level, and the kinetics of the processes dealt with require extensive study with the use of the most modern methods.

The dehydration of C_4–C_5 hydrocarbons at low pressures has been widely adopted in the synthetic rubber industry, and a tendency has been noted to extend work still further in the field of single-stage dehydrogenation under vacuum of alkanes or mixtures of alkanes and alkenes to give alkadienes.

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CALCULATION OF THE ACTIVATION ENERGY OF CHEMICAL REACTIONS ON THE BASIS OF THE ADDITIVITY PRINCIPLE

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1. INTRODUCTION

A great mass of experimental data has now accumulated in the literature on chemical kinetics and urgently requires generalisation and classification. However, to appraise this mass of disconnected and often contradictory facts is quite a complex task, made difficult by the fact that the theoretical premises and the methods of calculation of the kinetic parameters for most chemical reactions are still in an "embryonic" state.

The now generally accepted theoretical treatment of the nature of the elementary act of a chemical reaction is based on the "activated complex" method developed by Eyring[1] and by Evans and Polanyi[2]. It is based on the concept that the configuration of the atoms of a system, whilst changing continuously during the course of a reaction, passes through some critical intermediate configuration, which has received the name of "activated complex" or "transition state". A quite important concept introduced in this method is the potential-energy surface with a saddle point corresponding to the "transition state". The height of this point in comparison with the initial system gives the activation energy of the chemical reaction.

In its quantitative aspect the activated complex method frequently allows the pre-exponential factors in the Arrhenius equation to be calculated satisfactorily[3]. The accuracy of the results thus obtained is approximately one order of magnitude.

As regards calculations of activation energy, the results obtained so far have been much more modest. The most developed theory is that for the simplest system of three hydrogen atoms, which corresponds to reaction (1):

$$H\cdot + H_2 \rightarrow H_2 + H\cdot \qquad (1)$$

Many studies[4-12] have been devoted to quantum-mechanical calculations of system (1), but it is only very recently that the use of computer techniques has allowed agreement

with the experimental results to be reached[12]: the calculated value is $E = 6.2$ kcal†, and the experimental activation energy is ~7 kcal.[13]

The difficulty of direct quantum-mechanical calculations of activation energy stimulated the creation of the so-called "semiempirical" method, proposed by Eyring and Polanyi[13] and somewhat modified by Sato[14]. In this method the well-known London formula for the energy of a three-electron system[15] is used in conjunction with empirical curves of the Morse type for the potential energy of diatomic molecules[16]. However, here agreement with experiment is reached by the introduction into the formulae of an arbitrary parameter, the value of which is selected to "fit" the calculated activation energy to the experimental value. Hence "the semiempirical method introduces considerable uncertainty into activation energy calculations, in which it is material that the inaccuracy in the determination of E is theoretically completely uncontrollable"[17].

Matters are even worse for multi-electron atoms and molecules, especially when p-electrons participate in the elementary act. Here the picture of the interaction is complicated by the specific arrangement of the electron clouds and the transfer to this system of the conclusions and analyses made on the basis of the semiempirical method for 1s-electrons is quite inadmissable.

Hence the problem of the direct theoretical calculation of the activation energy of chemical reactions remains unsolved. Because of this, various empirical relations between activation energies and various factors characterising the reacting molecules or radicals have become important. These relations connect indirectly the rate of a chemical reaction with the structure of the molecule and the thermodynamics of the reaction. The clearest connection between the activation energy E and the exothermicity ΔH is for radical substitutions of type (2):

$$R\cdot + R'X \rightarrow RX + R'\cdot \qquad (2)$$

It was found empirically[17-21] that on changing either R or R′ the value of E is a linear function of ΔH (Polanyi's rule). This makes it possible to express the dependence of E on ΔH in the following generalised form:

$$E = a + b\Delta H \qquad (3)$$

where a and b are constants for a given homologous series.

By generalising much experimental material, Semenov[17] concluded that Eqn. (3) can be written in the form (4) with sufficient approximation:

$$E = 11.5 - 0.25\,\Delta H \qquad (4)$$

for exothermic reactions, and as (4′) for endothermic:

$$E = 11.5 + 0.75\,\Delta H. \qquad (4')$$

Relations (4) and (4′) allow the activation energy of radical reactions to be evaluated with an accuracy of 2–3 kcal. These relations are satisfactory for various atoms and radicals, but not for halogen atoms and reactions of type (1) involving H and D atoms. However, since the reactions which satisfy this relation are all radical reactions there is great interest in seeking more general relationships which are applicable to a wider class of reactions, both radical and molecular.

† For brevity, here and subsequently we write kcal instead of kcal mole^{-1}.

The principles described below allow the activation energy of the most varied reactions, both radical and molecular, to be determined with good accuracy.

2. STRUCTURE OF ACTIVATED COMPLEXES OF CHEMICAL REACTIONS

The principal feature of every chemical reaction is that during it some chemical bonds are broken and others are formed. In homolytic reactions the breaking of the bonds takes place in such a way that the atoms which form the bond do not acquire electrical charges. This signifies that the electron pair of the chemical bond is divided and each electron remains at its "own" atom. Consequently, in the rupture of every chemical bond two free valencies arise, which can either be used in the same elementary act for the formation of other bonds, or remain unutilised.

The breaking of some and the formation of new bonds proceeds gradually during the continuous change of the coordinates of the atoms in the system. The energy maximum of the system corresponds to the transition state, in which there are weakened breaking bonds and also even weakened new bonds. Hence in the activated complex instead of the bonds which are being broken and formed we have other weaker bonds, which we will conventionally term "activated" subsequently.

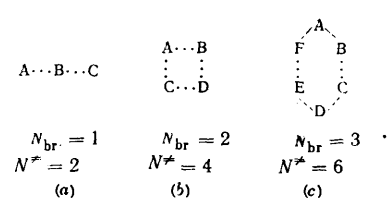
To understand the nature of the elementary chemical act it is necessary to find the structure of the activated complex. For radical reactions (2) the activated complex has the form A...B...C, where the dots denote activated bonds. For molecular reactions of a different type four-membered and six-membered cyclic complexes have been proposed[22]. Hence the number of activated bonds can be different. When the valency of the atoms of a system is constant, it can be shown that the number of activated bonds satisfies the following simple relationship:

$$N^{\neq} = 2N_{br} - \frac{\Delta n}{2} \qquad (5)$$

where N_{br} is the number of bonds broken during the course of the reaction, and Δn the change in the number of free valencies.

From this relation clearly Δn is always even, that is, only pairs of free valencies can appear or disappear during the course of the reaction. When there is a single free valency in the initial system then it cannot disappear (the "indestructibility of the free valency").

Let us consider what happens with $\Delta n = 0$. Here $N^{\neq}$ equals 2, 4, and 6 for $N_{br} = 1$, 2, and 3 respectively. The structure of the activated complexes for these instances is shown in scheme (A):



(A)

Activated complex (*a*) corresponds to radical reactions, (*b*) and (*c*) to molecular ones.

For $\Delta n \neq 0$ two variants are most frequently encountered: $N_{br} = 1$, $\Delta n = \pm 2$ [scheme (B)]:

$$\begin{array}{cc} A\cdots B & \begin{array}{c} A\cdots B \\ \diagdown C \diagup \end{array} \\ \Delta n = 2 & \Delta n = -2 \\ N^{\neq} = 1 & N^{\neq} = 3 \\ (d) & (e) \end{array} \qquad (B)$$

Activated complex (*d*) corresponds to dissociation of the molecule into two radicals, (*e*) to the reaction of the molecule with a biradical.

In the schemes shown for the activated complexes the species A, B, etc. can be either atoms or radicals consisting of a few atoms.

The schemes described include only activated bonds. In reality, in addition to these bonds the activated complex also has ordinary chemical bonds which enter into the composition of the reacting components A, B, etc. However, only the activated bonds determine whether chemical reactions occur since the other bonds are unchanged during the course of the reaction.

Hence the structure of the activated complex can be represented in the usual way employed for molecules. The main differences are that activated bonds denoted by dots are much weaker than chemical bonds and their number does not obey the usual valence rules. These differences arise because the activated bond is not the usual two-electron bond. It is easily seen that the total number of electrons participating in all the activated bonds is:

$$m = 2N_{br} + n_0$$

where n_0 is the number of unpaired electrons of the initial system which participate in the reaction, and therefore the number of electrons taking part in one activated bond does not equal zero in the general case. However, despite the major difference in the nature of the activated and ordinary chemical bonds, the above method of representing the structure of the activated complex gives good results and (as will be shown later) allows the activation energies of the most diverse chemical reactions to be calculated with reasonable accuracy.

3. ADDITIVITY OF THE ENERGY OF AN ACTIVATED COMPLEX

The principle of the additivity of the bond energies of the atoms in molecules is well-known; according to it the atomisation energy of a molecule equals the sum of the mean energies of the bonds between the various atoms:

$$V = \sum Q. \qquad (6)$$

This principle allows the heats of various types of chemical reaction and certain thermodynamic properties of substances to be calculated.

From the theoretical standpoint the validity of the additivity principle signifies that the interaction of the atoms which are not directly connected to one another can be neglected. This possibility is not obvious.

On considering a molecule as a multi-electron system and rigorously solving the corresponding Schrödinger equation, we also have to include in the Hamiltonian operator terms which describe the interaction of electrons belonging to different valence bonds. It is known[23] that allowance for this interaction leads to an increase in the energy of the system, in other words, electrons which are not paired with one another are repulsed. Under certain assumptions the energy of the molecule can be represented[24] by the approximate additive formula:

$$E = \sum Q_{ij} + \sum A_{ii} - \frac{1}{2}\sum_{i \neq j} A_{ij} \qquad (7)$$

where Q_{ij} is the coulombic energy of all the electron pairs, A_{ii} the exchange energy of the paired electrons which form the bond, A_{ij} the exchange energy of pairs of electrons which do not form a bond.

In Eqn. (7) there are terms which describe the interaction of electrons of different valence bonds. Hence quantum mechanics leads with known approximation to the idea of the additivity of the energy of the molecule, but with allowance for the repulsion of non-bonded atoms. The fact that the usual additive scheme for the calculation of energy gives good results is evidence that these additional terms can be neglected.

Note that there is a class of molecules where the atoms which are not directly connected have a quite significant effect—these are the molecules with conjugated multiple bonds. Conjugation lowers the energy of the molecule and in Eqn. (6) it is then necessary to introduce a corresponding correction allowing for the presence of conjugation[25]:

$$V = \sum Q + \Delta Q_{conj}.$$

Another factor which greatly affects the energy of certain molecules is the deformation of the valence angles in cyclic structures. This increases the energy of the molecule and in Eqn. (6) it is necessary to introduce the deformation energy (strain energy)[26]:

$$V = \sum Q - \Delta Q_{def}.$$

An analysis of many experimental results on the chemical kinetics led us to conclude that the additivity principle can be extended to the bond energies of the atoms in the activated complex[27,28]. This makes it possible to calculate the activation energy of a variety of chemical reactions.

For the change from the initial system to the activated complex energy equal to ΣQ_{br} must be expended in breaking some of the chemical bonds. During this, activated bonds are formed and energy is released, equal to $\Sigma Q^{\neq}$. Therefore the activation energy of the chemical reaction, which is equal to the energy expended in going from the initial system to the activated complex, can be represented by the following equation:

$$E = \sum Q_{br} - \sum Q^{\neq}; \qquad (8)$$

in other words, the activation energy equals the sum of the energies of bonds which are broken minus the sum of the energies of the activated bonds.

Eqn. (8) is applicable both for the forward and for the reverse reaction. Since the activated complex for the elementary acts of the forward and reverse reactions is the same, the corresponding difference in activation energies will equal the difference between the energies of the bonds broken in the forward and reverse reactions, that is, the exothermicity:

$$E - E' = \sum Q_{br} - \sum Q'_{br} = \Delta H.$$

Eqn. (8) allows the activation energy of a chemical reaction to be calculated when the energies of the activated bonds are known.

The most rigorous path for the determination of the value of $Q^{\neq}$ consists in the direct quantum-mechanical calculation of the activated complex. However, as noted above, quantum chemistry has not yet achieved the necessary accuracy in calculating the activated complex in even the simplest instances.

Another way consists in using reliable experimental data on the kinetics of certain reactions to calculate the energies of the activated bonds by Eqn. (8). The energies of the activated bonds thus found allow the activation energies of many other chemical reactions to be calculated.

We show below the applicability of the additivity principle in the calculation of activation energies for radical reactions, and then also for molecular reactions. The necessity for considering radical and molecular reactions separately stems from the different requirements as regards the accuracy of the activation energy calculations. For molecular reactions, which usually have an activation energy E of between 20 and 65 kcal, an accuracy of 3–4 kcal in the calculation seems quite satisfactory. However, with radical reactions, for which a value of E of ~10 kcal or less is characteristic, it is desirable to carry out the calculations with an accuracy of ~1 kcal. This is also responsible for some differences in the corresponding calculation procedures.

Strictly speaking, Eqn. (8) gives us an expression for the "microscopic" activation energy, determinable as the difference in the zero energy levels of the activated complex and the initial system. In practice, however, we will be dealing with experimental activation energies determinable from the slope of the curve giving the temperature dependence of the reaction rate constant in Arrhenius coordinates.

As Temkin has shown[29], the experimental activation energy corresponds to the statistical determination of this quantity as the difference between the mean energies of the reacting molecules and the initial ones. At moderately high temperatures the "microscopic" and "statistical" activation energies are almost the same. The difference between them—a quantity of the order of RT—usually lies within the limits of experimental error. Therefore subsequently we will assume that the experimental activation energy is equal to the energy barrier of the reaction.

4. RADICAL SUBSTITUTIONS

For the radical substitution (9):

$$R\cdot + R'X \rightarrow RX + R'\cdot \qquad (9)$$

the activated complex, which is of the form R...X...R', belongs to type (*a*) (see p. 512). In this reaction one chemical bond is broken, R'–X, and in the activated complex there are two activated bonds, R...X and R'...X.

Before turning to the calculation of activation energy, we will give the following definition: the energy for the breaking of an activated bond $Q_{R\ldots X}$ is that part of the heat change $D_{R\ldots X\ldots R'}$ of the dissociation of the activated complex with formation of the free radicals R' and R'' and the atom X at 0°K in the gas phase which is associated with one activated bond:

$$R\ldots X\ldots R' \rightarrow R\cdot + X + R'\cdot \qquad (10)$$

Since in this reaction there is the simultaneous breaking of two activated bonds, the above definition is actually within the framework of our postulated principle for the additivity of the activation energy of the complex. The essense of this principle comprises the following two assumptions:

1. The energy for the dissociation of the activated complex equals the sum of the energies for the breaking of the activated bonds:

$$D_{R\ldots X,\ldots R'} = Q_{R\ldots X} + Q_{R'\ldots X}. \qquad (11)$$

2. The energy for the breaking of an activated bond $Q_{R\ldots X}$ is independent of the radical R'' and is therefore constant and characteristic of the RX molecule.

These assumptions are generally true only to a certain approximation. The nature of a substituent can influence to a certain extent the bond energies of the atoms in the molecule. Hence the nature of the radical R'' can change the energy of the activated bond $Q_{R\ldots X}$ within certain limits. However, we assume that this influence is small and can be allowed for in the appropriate way.

To calculate the activation energy of reaction (9) it is necessary to know the energy consumed in going from the initial system to the activated complex. For this purpose we will divide this change into two stages. First let the chemical bond R'–X be broken with the formation of atom X and radical R''. Then let a reaction take place, the reverse of reaction (10). In this, the energy released is equal to $D_{R\ldots X\ldots R'}$. Hence the activation energy of reaction (9) is

$$E = Q_{R'-X} - (Q_{R\ldots X} + Q_{R'\ldots X}) \qquad (12)$$

which agrees with general Eqn. (8). However, it must be remembered that the quantities in Eqn. (12) are energies for the breaking of bonds.

For the reverse reaction the activation energy is expressed by a similar relation:

$$E' = Q_{R-X} - (Q_{R\ldots X} + Q_{R'\ldots X})$$

so that the difference in these quantities:

$$E - E' = Q_{R'-X} - Q_{R-X} = \Delta H$$

equals the heat of reaction.

To calculate the activation energy by Eqn. (12) the energies of the activated bonds $Q_{R\ldots X}$ and $Q_{R'\ldots X}$ must be known. These quantities can be determined with the aid of the same equation from experimental data on the activation energies of certain reactions[27]. Table 1 gives the energies thus calculated for some activated bonds, together with the corresponding experimental data used for the calculations.

Note that to calculate each of the quantities $Q_{R\ldots X}$ the experimental value of the activation energy of the corresponding reaction is used. Consequently the accuracy of the calculation of $Q_{R\ldots X}$ depends on the reliability of the experimental results used. Therefore the quantities used in Table 1 are not, strictly speaking, definitive and could be refined subsequently.

The values given in Table 1 for the energies of the breaking of the bonds in molecules are recommended for use in calculating activation energy, since these particular values are used for calculating the energies for the breaking of activated bonds.

An illustration of the applicability of Eqn. (12) for calculating the activation energy of radical reactions is given by Table 2, in which calculated activation energies are compared with corresponding published values. Clearly,

TABLE 1. Energies for the breaking of bonds in molecules and activated complexes at 0°K.

Bond	Q_{R-X}, kcal	Ref.	$Q_{R\ldots X}$, kcal	Calculated for the reaction	E_{expt}, kcal	Ref.
H...CH_3	101 5	32	43.6	$CH_3+CH_4 \rightarrow CH_4+CH_3$	14.3	38
H...C_2H_5	97 0	30	43.0	$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5$	10.4	39
H...C_{prim}	94.9*		41.3	$CH_3+(CH_3)_4C \rightarrow CH_4+(CH_3)_3CCH_2$	10.0	39
H...C_{sec}	92.0*		40.3	$CH_3+n\text{-}C_5H_{12} \rightarrow CH_4+C_5H_{11}$	8.1	39
H...C_{tert}	87.2*		36.0	$CH_3+iso\text{-}C_4H_{10} \rightarrow CH_4+C_4H_9$	7.6	39
H...H	103.3	32	44.3	$H+C_2H_6 \rightarrow H_2+C_2H_5$	9.7	62
H...OH	118.0	32	48.5	$OH+C_2H_6 \rightarrow H_2O+C_2H_5$	5.5	45
H...O	101.4	32	47.5	$O+n\text{-}C_4H_{10} \rightarrow OH+C_4H_9$	4.2	42
H...NH_2	104.0	32	50.6	$CH_3+NH_3 \rightarrow CH_4+NH_2$	9.8	51
H...CH_3CO	79 0	30	27.9	$CH_3+CH_3CHO \rightarrow CH_4+CH_3CO$	7.5	52
H...CF_3	101.0	32	46.5	$CF_3+C_2H_6 \rightarrow CF_3H+C_2H_5$	7.5	49
H...$C_6H_5CH_2$	83.0	30	31.1	$CH_3+C_6H_5CH_3 \rightarrow CH_4+C_6H_5CH_2$	8.3	39
H...CH_2–CH=CH_2	77.0	30	25.7	$CH_3+C_3H_6 \rightarrow CH_4+C_3H_5$	7.7	39

* Calculated by Voevodskii's formula[31] for propane and isobutane.

TABLE 2. Activated energies of radical reactions.

Reaction	E_{calc}, kcal	E_{expt}, kcal	Ref.
$H+CH_4 \rightarrow H_2+CH_3$	13.6	13.0	59
$H+C_3H_8 \rightarrow H_2+C_3H_7$	7.4	8.2	33
$H+n\text{-}C_4H_{10} \rightarrow H_2+s\text{-}C_4H_9$	7.4	7.1	34
$H+iso\text{-}C_4H_{10} \rightarrow H_2+(CH_3)_3C$	6.9	6.8	35
$H+(CH_3)_4C \rightarrow H_2+(CH_3)_3CCH_2$	9.3	9.3	36
$H+CH_3CHO \rightarrow H_2+CH_3CO$	6.8	6.0	37
$CH_3+C_2H_6 \rightarrow CH_4+C_2H_5$	8.1	8.0	39
$CH_3+n\text{-}C_4H_{10} \rightarrow CH_4+s\text{-}C_4H_9$	8.1	8.1	39
$CH_3+n\text{-}C_6H_{14} \rightarrow CH_4+s\text{-}C_6H_{13}$	8.1	8.1	39
$CH_3+(CH_3)_3CC(CH_3)_3 \rightarrow CH_4+(CH_3)_3CC(CH_3)_2CH_2$	10.0	9.5	39
$CH_3+(CH_3)_2CHCH(CH_3)_2 \rightarrow CH_4+(CH_3)_2CHC(CH_3)_2$	7.6	7.8	39
$CH_3+(CH_3)_2CHCH(CH_3)CH(CH_3)_2 \rightarrow CH_4+(CH_3)_2CCH(CH_3)CH(CH_3)_2$	7.6	7.9	39
$CH_3+\Delta\text{-}C_6H_{12} \rightarrow CH_4+\Delta\text{-}C_6H_{11}$	8.1	8.3	39
$O+H_2 \rightarrow OH+H$	11.5	11.7	53
$O+CH_4 \rightarrow OH+CH_3$	10.4	8.7	40
$O+C_2H_6 \rightarrow OH+C_2H_5$	6.5	7.5	41
$O+\Delta\text{-}C_6H_{12} \rightarrow OH+\Delta\text{-}C_6H_{11}$	4.2	4.5	55
$O+CH_3CHO \rightarrow OH+CH_3CO$	3.6	3.0	43
$O+NH_3 \rightarrow OH+NH_2$	5.9	4.9	54
$OH+H_2 \rightarrow H_2O+H$	10.5	10.0	56
$OH+CH_4 \rightarrow H_2O+CH_3$	9.4	9.0	44
$OH+CH_3CHO \rightarrow H_2O+CH_3CO$	2.6	4.0	46
$CF_3+CH_4 \rightarrow CF_3H+CH_3$	11.4	11.0	47
$CF_3+C_3H_8 \rightarrow CF_3H+iso\text{-}C_3H_7$	5.2	6.2	48
$CF_3+n\text{-}C_4H_{10} \rightarrow CF_3H+s\text{-}C_4H_9$	5.2	5.3	48
$CF_3+(CH_3)_4C \rightarrow CF_3H+(CH_3)_3CCH_2$	7.1	7.6	48
$CF_3+iso\text{-}C_4H_{10} \rightarrow CF_3H+(CH_3)_3C$	4.7	4.7	49
$CF_3+C_6H_5CH_3 \rightarrow CF_3H+C_6H_5CH_2$	5.4	5.4	50
$CF_3+\Delta\text{-}C_6H_{10} \rightarrow CF_3H+\Delta\text{-}C_6H_9$	5.1	4.7	48

the difference between the calculated and experimental values usually does not exceed 0.5–0.7 kcal.

If it is assumed that the accuracy of the experimental determination of activation energies of radical reactions is comparatively moderate (1–2 kcal), the approximation obtained must be considered good.

The additivity rule is obeyed by the reactions of various radicals with the most varied molecules. Exceptions are the reaction of free halogen atoms and reactions of type (1) with the participation of H and D atoms. It is remarkable that these particular reactions do not obey the Semenov relation. Possibly, here the direct interaction of radicals R and R′, not allowed for in Eqn. (12), is significant.

It is interesting to note that there is a clear linear correlation between the energies of breaking of the activated and the ordinary chemical bond (Fig. 1). The dependence of $Q_{R\ldots H}$ on Q_{R-H}, where R is a hydrocarbon radical, can be expressed by the simple relation:

$$Q_{R\ldots H} = 0.83\,(Q_{R-H} - 45)\ \text{kcal}\ . \qquad (13)$$

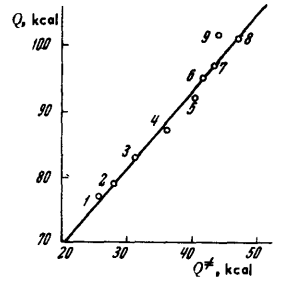


Fig. 1. Relation between the energies for breaking bonds between the atoms in the molecule and in the activated complex of radical reactions:
1) H–C_3H_5; 2) H–CH_3CO; 3) H–$C_6H_5CH_2$; 4) H–t-C_nH_{2n+1}; 5) H–s-C_nH_{2n+1}; 6) H–n-C_nH_{2n+1} ($n \geq 3$); 7) H–C_2H_5; 8) H–CF_3; 9) H–CH_3 (from the data of Table 1).

This relation allows the energy of an activated bond to be evaluated approximately in those instances when the experimental data needed for more accurate calculation are not available.

Note, however, that the accuracy of the results obtainable in this calculation (2–3 kcal) is somewhat worse than when using tabulated data.

Relation (13) agrees with the Polanyi rule and with the Semenov relation. In this connection we will examine several reactions in which radical R is changed but the R′X molecule remains the same. On substituting Eqn. (13) for $Q_{R\ldots X}$ and $Q_{R'\ldots X}$ in Eqn. (12) we obtain:

$$E = A - 0.17\Delta H, \qquad (14)$$

where $A = 74.7 - 0.66Q_{R-X}$.

We have arrived at a relation close to that of Semenov, Eqn. (4). Since $Q_{R\ldots X}$ for alkanes has a value of ~90 to 100 kcal, here A = 9–15 kcal.

An interesting feature of Eqn. (14), equally true of the Semenov relation (4), is that since the coefficient of ΔH is small, change in energy of the bond being broken (or the heat of reaction) has comparatively little effect on the value of the activation energy.

However, for the same reason the use of these relations for the reverse calculation of thermal effects (or bond energies) with the aid of data on activation energies leads to considerable errors. For example, an inaccuracy in Eqn. (14) of 3 kcal gives an error of ~18 kcal in the determination of ΔH. Therefore in using relations (4) and (14) extreme care must be taken and it can only be used for direct calculations of activation energy.

5. ACTIVITY OF RADICALS AND MOLECULES

From the above, three quantities must be known to calculate the activation energy of radical reactions: $Q_{R'-X}$, $Q_{R\ldots X}$, and $Q_{R'\ldots X}$.

However, often all these quantities are unknown. Therefore there is interest in those modifications of the additivity principle which would allow less information to be used. The following two corollaries of Eqn. (12) are useful for this purpose.

First corollary (relative activities of radicals). Let us consider two reactions for different radicals R_1 and R_2 with the same substance RX. The activation energies of these reactions, according to Eqn. (12), are:

$$E_1 = Q_{R-X} - (Q_{R_1\ldots X} + Q_{R\ldots X})$$
$$E_2 = Q_{R-X} - (Q_{R_2\ldots X} + Q_{R\ldots X}).$$

On subtracting one equation from the other we obtain:

$$E_1 - E_2 = Q_{R_2\ldots X} - Q_{R_1\ldots X}. \qquad (15)$$

In other words, *the difference in the activation energies for the reactions of two given radicals* R_1 *and* R_2 *with the same substance* RX *is independent of the nature of this substance and is a constant quantity*. This difference is determined by the energies of the activated bonds $Q_{R_1\ldots X}$ and $Q_{R_2\ldots X}$, and the greater the energy of the activated bond the less the activation energy.

Hence the energy of an activated bond can serve as a quantitative characteristic of the activity of a given radical. If we conventionally take the activity of any one radical (for example, CH_3) as zero, then the difference $Q_{R_i\ldots X} - Q_{CH_3\ldots X}$, or the equal difference between the corresponding activation energies, will characterise the *relative* activity (α) of the radicals in comparison with the radical CH_3. By the relative activity of a radical (in relation to CH_3) we understand the difference between the activation energies of the reactions of CH_3 and this radical with the same substance.

Table 3 gives a series of radicals in order of increasing activity. The relative activities in this table were calculated from the data in Table 1.

It must be pointed out that this determination of the relative activity of radicals differs from Semenov's proposal[17]. By relative activity this author[17] means the difference in the heats of the corresponding reactions, and not the difference in activation energies.

Naturally, between these two determinations‡ it is easy to find an unambiguous relation according to Polanyi's rule since the series of radical activities given in Table 3 can in principle be obtained from the corresponding Semenov series.

An illustration of the accuracy which is achieved with the first corollary of the additivity principle is provided in Table 4, which gives published data on the reactions of the hydrogen atom and the CF_3 radical with various substances. Obviously the difference $E_1 - E_2$ is constant with an accuracy of 0.2–0.3 kcal and agrees with that calculated in Table 3.

TABLE 3. Relative activity of radicals in reactions of the type $R_i + RH \rightarrow R_iH + R$.

Radical R_i	$CH_2{=}CH{-}CH_2$	$C_6H_5CH_2$	C_6H_5	CH_3	H	CF_3	O	OH
Relative activity, α	—17.9	—12.5	—0.6	0	0.7	2.9	3.9	4.9

‡ Semenov also mentioned[17] the possibility of compiling series of activities of free radicals from activation energies (as has been done by the author of this review) (Russian editorial note).

TABLE 4. Activation energies for the reactions of H· and CF_3 with various substances.

Substance	$H + RH \rightarrow H_2 + R$		$CF_3 + RH \rightarrow CF_3H + R$		$E_1 - E_2$
	E_1	Reference	E_2	Reference	
C_2H_6	9.7	62	7.5	49	2.2
C_3H_8	8.2	33	6.2	48	2.0
$n\text{-}C_4H_{10}$	7.1	34	5.3	48	1.8
$iso\text{-}C_4H_{10}$	6.8	35	4.7	49	2.1
$(CH_3)_4C$	9.3	36	7.6	48	1.7
CH_3COCH_3	9.0	57	6.9	58	2.1

By using the relative activities of the radicals, the activation energies of reactions of a given radical with any substance can be calculated if the activation energy of the reaction of another radical with the same substance is known:

$$E_1 = E_2 + \alpha_2 - \alpha_1.$$

For calculation by this equation only one quantity E_2 need be known.

The series of relative activities of the radicals can be quite useful for classifying the available experimental data on the kinetics of radical reactions. It allows the reliability of the available data to be evaluated and clearly unreliable values to be rejected. An important point is that in this method it is necessary to have the minimal information, namely: the value of only one activation energy of any radical of this series with the substance of interest. From this standpoint the second corollary is quite useful.

Second corollary (relative reactivities of substances). Let us consider two reactions of a single radical R with two different molecules R_1X and R_2X. The activation energies of these reactions, according to the additivity principle, are:

$$E_1 = Q_{R_1-X} - (Q_{R\ldots X} + Q_{R_1\ldots X})$$
$$E_2 = Q_{R_2-X} - (Q_{R\ldots X} + Q_{R_2\ldots X}).$$

Subtracting one equation from the other, we obtain

$$E_1 - E_2 = Q_{R_1\ldots X} - Q_{R_1\ldots X} - (Q_{R_2-X} - Q_{R_2\ldots X}) \qquad (15a)$$

that is, *the difference in the activation energies of reactions of the same radical with two given substances is independent of the nature of this radical and is a constant*, which can be determined solely by the quantities characteristic for the molecules taken: $Q_{R-X} - Q_{R_1\ldots X}$.

The values of $Q_{R_i-X} - Q_{R_i\ldots X}$ can therefore serve as a quantitative characteristic of the reactivity of a given substance. If it is conventionally assumed that the reactivity of one particular substance (for example, H_2) equals zero, then the difference of corresponding activation energies gives the *relative* reactivity of the different substances in comparison with hydrogen. Hence by the relative reactivity of a given substance (relative to H_2) we mean the difference between the activation energies for the reaction of H_2 and of this substance with the same radical.

As for the activity of the radicals, our determination of the relative reactivity differs from Semenov's proposal[17]; however, Polanyi's rule here allows us to establish a single-valued relation between them.

Table 5 gives a series of relative reactivities β for certain substances which we have obtained from an analysis of many experimental results, including those given in Table 2.

TABLE 5. Relative reactivity of R_iH molecules in reactions of the $R + R_iH \rightarrow RH + R_i$ type (kcal).

Substance R_iH	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_6	CH_3CHO
Relative reactivity, β	0	1.0	4.6	5.6	6.7	7.3	7.8

TABLE 6. Activation energy for various radicals with CH_4 and C_2H_6.

Radical, R	$R+CH_4 \rightarrow RH+CH_3$		$R+C_2H_6 \rightarrow RH+C_2H_5$		$E_1 - E_2$, kcal
	E_1, kcal	Reference	E_2, kcal	Reference	
H	13.0	59	9.7	32	3.3
OH	9.0	45	5.5	45	3.5
CH_3	14.3	38	10.4	39	3.9
CN	—	—	—		3.7 [60]
CF_3	11.0	47	7 5	49	3.5

Table 6 gives published data which illustrate the second corollary of the additivity principle. They suggest that the difference in activation energies of the reactions of CH_4 and C_2H_6 molecules with various radicals is constant, irrespective of the nature of the radical, and agrees within 0.2–0.3 kcal with the value $E_1 - E_2 = 3.6$ kcal calculated from the data of Table 5.

By using a series of relative reactivities β_i of substances the activation energy for the reaction of a given radical with any substance can be calculated when the activation energy of a reaction of this radical with even a single substance of this series is known:

$$E_1 = E_2 + \beta_2 - \beta_1.$$

It is necessary to know only one value E_2 for calculation by this relation. A series of relative reactivities can be useful for a comparative evaluation of experimental data from the reactions of one radical with different molecules.

6. MOLECULAR REACTIONS

The additivity principle postulated for radical reactions can be extended to the reactions of saturated molecules. This makes it easy to calculate the activation energies of corresponding reactions. Such calculations are especially important since in distinction from radical reactions molecular reactions have as yet no relations for evaluating the activation energy. The existing theories of the rate of molecular reactions [61] in essence do not even mention the problem of the calculation of activation energy and only discuss the possibility of determining the pre-exponential factors.

The activated complex of most molecular reactions belongs to one of two types (*b*) and (*c*) (see scheme A), that is, in these reactions two or three chemical bonds are broken and four or six activated bonds respectively are formed.

The activated bond energies needed for calculating the values of E by Eqn. (8) can be determined with the aid of reliable experimental data on the kinetics of certain reactions.

Since in molecular, as opposed to radical, reactions several chemical bonds are broken simultaneously it is desirable to use the mean energies of the bonds between atoms of different elements. This somewhat reduces the accuracy of the calculation but considerably broadens the region of its use.

Table 7 gives the mean bond energies of the atoms in the molecules at 0°K and the corresponding mean energies of the activated bonds. The values of Q are taken from Moelwyn-Hughes [63], but we have rounded them off to whole numbers to simplify the calculations. Naturally, these quantities are not sufficiently precise and their value can be judged solely from how well they allow the activation energies of chemical reactions to be calculated.

Just as for molecules, the mean energy of an activated bond is that part of the heat of atomisation of an activated complex associated with one activated bond. When there are ordinary chemical bonds as well as the activated bonds in the activated complex then in the calculation of the heat of atomisation they are given the mean energies of bonds in molecules.

Hence we will use Eqn. (8) to calculate the activation energies of molecular reactions, taking Q_{br} and $Q^{\neq}$ in this equation to be *mean* bond energies, with one exception, which will be mentioned below. As stated above, the deformation of valence angles in rings leads to a departure from additivity by the strain energy of the ring:

$$V = \sum Q - \Delta Q_{def.} \qquad (16)$$

Because of this the energy for the rupture of a C–C bond in rings is considerably less than the mean energy of a C–C bond in alkanes; it is 50, 60, and 72 kcal for cyclopropane, cyclobutane, and cyclopentane, respectively [26]. This shows that the equality

$$Q_r \simeq Q - \Delta Q_{def.}$$

where Q_r is the energy of rupture of the C–C bond in cyclanes, is obeyed with sufficient accuracy for our purposes.

TABLE 7. Mean bond energies in molecules and activated complexes at 0°K.

Bond	Q, kcal	$Q^{\neq}$, kcal
H—H	103	45
C—H	99	45
σ– C—C in alkanes	79	28
π– C ⋯ C in alkenes	61	17
π– C ⋯ C in acetylene	56	9
σ– C—O	80	18
π–C ⋯ O	88	27
O—H	105	55
C_{prim}—Cl	76	18
C_{sec}—Cl		25
C_{tert}—Cl		32
C_{prim}—Br	63	16
C_{sec}—Br		21
C_{tert}—Br		26
C_{prim}—I	47	8
C_{sec}—I		16
C_{tert}—I		24
H—Cl	102	40
H—Br	87	33
H—I	70	23
Correction for conjugation $\Delta Q^{\neq}_{conj.}$	—	12

Then Eqn. (16) can be written in the form

$$V = \sum_{n-1} Q + Q_r \qquad (17)$$

which is formally similar to the general equation (6), but in which one value of the mean energy is replaced by the bond rupture energy.

Hence if during the course of a reaction bonds forming part of a ring are broken then in Eqn. (8) for the calculation of E one energy of rupture of a C–C bond in a ring is substituted for the corresponding activated bond energy.

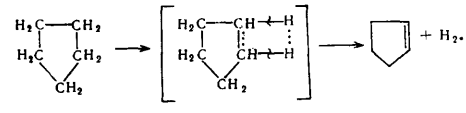
When there is a system of conjugated double bonds in an *activated complex* then the energy of *each* conjugated activated bond must be increased by the quantity $\Delta Q^{\neq}_{conj}$, equal to 12 kcal. Here it does not matter, to the first approximation, which double bonds are conjugated: C=C or C=O.

The author found the value of this correction, like the activated bond energies, by selection from many experimental results on kinetics. We do not make a correction for conjugation in the initial system since it is usually comparatively small and does not affect the calculated activation energy within the limits of error of the calculation.

As Fig. 2 shows, there is a linear relation between the energies of the C–H bonds in the molecules and in the activated complexes, in agreement with Eqn. (13). The existence of this relation allows the energy of the activated bonds to be determined when the energy of the bonds in the molecule differs considerably from the mean value shown in Table 7. For example, for activated bonds in cyclopropane, cyclobutane, and cyclopentane we obtain 4, 12, and 22 kcal respectively. In calculating activation energies it is recommended that the mean energies of the bonds of atoms in molecules given in Table 7 be used, since the activated bond energies found agree with these values.

We will illustrate the calculation of activation energies by examples.

1. The dehydrogenation of cyclopentane:

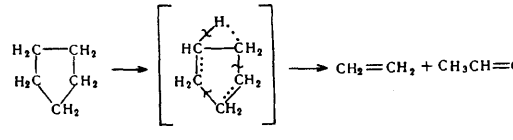


In this reaction two C–H bonds are broken and four activated bonds are formed: two C–H, one H–H, and one π-C–C. According to Eqn. (8) the activation energy is:

$$E = 2 \times 99 - (2 \times 45 + 45 + 17) = 46 \text{ kcal.}$$

The experimental value of E is 44 kcal.[64]

2. The decomposition of cyclopentane:



In this reaction three bonds are broken: two σ-C–C bonds in the five-membered ring and one C–H bond. In the activated complex there are six activated bonds: two C–H, two σ-C–C, and two π-C–C. Here the activated double bonds are conjugated.

$$E = 72 + 79 + 99 - (22 + 28 + 2 \times 45 + 2 \times 17 + 2 \times 12) = 52 \text{ kcal.}$$

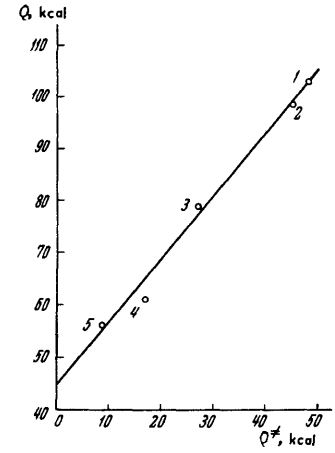
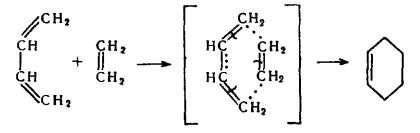


Fig. 2. Relation between the mean C–H bond energies in the molecule and activated complex for molecular reactions.

The experimental activation energy is 49.6 kcal.[64]

3. The Diels–Alder condensation:



During this reaction three π-C–C bonds are broken and a system of six activated bonds is formed: four π-C–C and two σ-C–C bonds. The three activated double bonds are conjugated:

$$E = 3 \times 61 - (4 \times 17 + 2 \times 28 + 3 \times 12) = 23 \text{ kcal.}$$

The experimental value of E is 26.7 kcal.[87]

In exactly the same way we calculated the activation energies of a large number of reactions of very different types. Table 8 gives the corresponding data.

These results show that calculated values of the activation energy agree well with the experimental values of E throughout the whole range of activation energies (25 to 70 kcal). The mean deviation does not exceed 2–3 kcal.

The additivity principle seems valid for reactions of the most varied types with molecules of different structure.

The additive scheme of calculating activation energy can be used for revealing the mechanism of a reaction and for obtaining a more accurate structure for the activated complex. A marked difference between the calculated and experimental activation energy suggests that the reaction does not proceed in the manner assumed. For example, in the decomposition of acetone under certain conditions the main products are keten and methane[99] and a molecular mechanism can be proposed for this reaction:

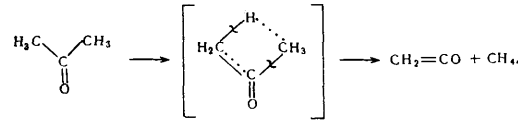
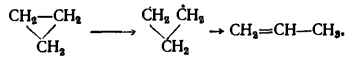


TABLE 8. Activation energies of molecular reactions.

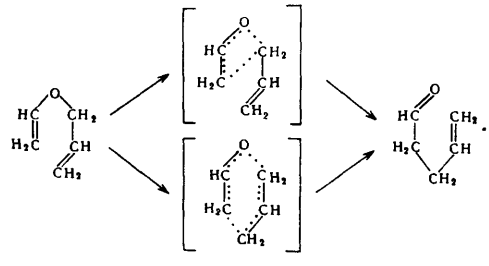
Reaction	E_{calc}, kcal	E_{exp}, kcal	Ref.
Cyclopentane → H_2 + cyclopentene	46	44.0	64
Cyclopentane → C_2H_4 + C_3H_6	52	49.6	64
d-Pinene → dipentene	43	43.7	65
Vinylcyclopropane → cyclopentene	51	50	66
Ethyl acetate → C_2H_4 + CH_3COOH	44	47.8	67
Isopropyl acetate → C_3H_6 + CH_3COOH	44	45	70
Ethyl formate → C_2H_4 + HCOOH	44	44.1	70
Isopropyl formate → C_3H_7 + HCOOH	44	44	70
Ethyl propionate → C_2H_4 + C_2H_5COOH	44	48.5	69
Cyclobutene → buta-1,3-diene	34	32.5	68
1-Methylcyclobutene → 2-methylbuta-1,3-diene	34	35.1	71
1,2-Dimethylcyclobutene → 2,3-dimethylbuta-1,3-diene	34	36	72
Cyclobutane → $2C_2H_4$	65	62.5	73
Methylcyclobutane → C_2H_4 + C_3H_6	65	62	74
Isopropylcyclobutane → C_2H_4 + alkene	65	62.6	75
Isopropenylcyclobutane → C_2H_4 + diene	53	51	76
Isopropenylcyclobutane → 1-methylcyclohexene	47	51	76
1-Chloroethane → HCl + C_2H_4	55	56.6	77
1-Chloropropane → HCl + C_3H_6	55	55	78
2-Chloropropane → HCl + C_3H_6	48	50.5	79
2-Chlorobutane → HCl + C_4H_8	48	49.6	80
2-Chloro-2-methylpropane → HCl + isobutene	41	41.4	81
Allyl vinyl ether → pent-4-enal	30	30.6	82
Allyl isopropenyl ether → allylacetone	30	29.3	83
CH_2=CH–O–C_2H_5 → C_2H_4 + CH_3CHO	47	43.8	84
CH_2=CH–O–$CH(CH_3)_2$ → C_3H_6 + CH_3CHO	47	43.6	85
3,7-Dimethylocta-1,6-diene → 3-isopropyl-1,2-dimethylcyclopentane	34	35.2	86
1,3-Butadiene + C_2H_4 → cyclohexene	23	26.7	87
2(Buta-1,3-diene) → vinylcyclohexene	23	23.1	88
2(Penta-1,3-diene) → dimer	23	25.4	89
Hepta-1,5-diene → 3-methyl-1,5-hexadiene	29	32.5	90
1-Bromoethane → HBr + C_2H_4	51	52.3	91
1-Bromopropane → HBr + C_3H_6	51	50.7	92
2-Bromopropane → HBr + C_3H_6	46	47.8	93
2-Bromo-2-methylpropane → HBr + isobutylene	41	41.0	94
1-Iodoethyl → HI + C_2H_4	53	53.7	95
2-Iodopropane → HI + C_3H_6	45	45.3	96
2-Iodobutane → HI + C_4H_8	45	47.9	97
2-Iodo-2-methylpropane → HI + isobutylene	37	36.4	98

However, the activation energy calculated by this mechanism (43 kcal) differs considerably from the experimental value (68 kcal), which compels us to reject the molecular mechanism in favour of a chain mechanism with loss of CH_3 as the first stage.

An analogous picture is observed for the isomerisation of cyclopropane into propene. The activation energy calculated by an additive scheme for a molecular mechanism is 38 kcal. The experimental value of E = 65.0 kcal [100] differs considerably from the calculated value. Obviously here the reaction proceeds through the formation of an intermediate biradical:



In several instances the additivity principle allows one of several proposed activated complexes for a single reaction to be chosen. For example, for the isomerisation of allyl vinyl ether into pent-4-enal two activated complexes, four-membered and six-membered, can be written:



Calculation gives E = 51 kcal for the four-membered complex, and E = 30 kcal for the six-membered. The experimental value [82], E = 30.6 kcal, shows that the reaction proceeds by the second path.

7. NATURE OF THE ACTIVATED BOND

A characteristic feature of the above approach to the calculation of activation energy is the hypothesis that an activated complex can be considered as a molecule the atoms of which are linked to one another by activated bonds. It is essential that the activated bonds introduced in this way have constant energies and the energy of the transition state is obtained by simple summation of the energies of all the activated bonds. The theoretical interpretation of the additivity principle involves explaining the nature of the activated bond and developing methods of calculating it.

Within the framework of the Heitler–London approximate quantum theory the energy of a two-electron bond is given by the expression:

$$Q = A + \alpha \qquad (18)$$

where A and α are the coulombic and exchange integrals.

Since the activated bond, as we have seen, is not the ordinary two-electron bond it is interesting to find, from the standpoint of the Heitler–London theory, a corresponding expression for the energy of an activated bond.

For the radical reactions of substitution (9) the activated complex can be considered as a three-electron system with an energy expressed by the London formula:

$$V = A + B + C - \left\{\frac{1}{2}[(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\gamma-\alpha)^2]\right\}^{1/2}. \qquad (19)$$

On the other hand, according to Eqn. (11), Eqn. (20) is valid:

$$V = Q_{R\ldots X} + Q_{R'\ldots X}. \qquad (20)$$

The applicability of the additivity rule signifies that direct interaction of radicals R and R′ within the activated complex can be neglected (this is equivalent to the condition $C = 0$, $\gamma = 0$). Moreover, since the activated bonds are independent, for simplicity the radicals R and R′ can be put identical. Then $A = B$, $\alpha = \beta$, $V = 2Q_{R\ldots X}$, and from Eqn. (19) we obtain Eqn. (21):

$$Q_{R\ldots X} = A + 0.5\,\alpha. \qquad (21)$$

Here, as already shown [101], the curve giving the dependence of $A + 0.5\alpha$ on the interatomic distance shows a minimum at the point corresponding to the dimensions of the activated complex, which makes it possible in principle to calculate the length of the activated bond and consequently also the pre-exponential factor in the Arrhenius equation.

However, it is easy to show [102] that Eqn. (21) has a more general character and is applicable not only to a radical but also to molecular reactions, the activated complex of which can be considered as a multi-electron system, the energy of which is obtained by solution of the corresponding secular equation. In particular, for a four-membered complex of type (*b*), considered as a four-electron system, the same London equation can be written, in which $A = A_1 + A_2$; $B = B_1 + B_2$; $\alpha = \alpha_1 + \alpha_2$; $\beta = \beta_1 + \beta_2$.

The applicability of the additivity principle in this instance shows that the interaction of non-neighbouring

atoms can be neglected, that is, here also we have $C = 0$ and $\gamma = 0$. Assuming, as before, that all four activated bonds are identical, we obtain $A = 4A_1$, $V = 4Q^{\neq}$ and Eqn. (19) is changed into the following equation:

$$Q^{\neq} = A_1 + 0.5\,\alpha_1 .$$

which is identical with Eqn. (21).

For a six-membered complex the position is somewhat complicated by the absence of a clear analytical expression for the energy of a six-electron system. However, here it is possible to use the result of a calculation of the energy of a benzene molecule, where all six π-bonds are also identical. If the interaction of non-adjacent atoms is neglected, then for the energy of the system we have[103] Eqn. (22):

$$V = \sum A + 2.61\,\alpha . \qquad (22)$$

Since here the activated complex consists of six identical bonds, Eqn. (23) which is similar to that obtained earlier, is valid for $Q^{\neq}$:

$$Q^{\neq} = A + 0.435\,\alpha . \qquad (23)$$

Hence from the standpoint of the approximate quantum theory, which represents the energy of a chemical bond as the sum of coulombic and exchange integrals, the energy of an activated bond can be represented approximately by Eqn. (19). Since the exchange integral constitutes the main part of the energy of a covalent bond, an activated bond is considerably weaker than an ordinary one. It must also be borne in mind that the quantities A and α which enter into the expression of the energy of an activated bond have another (lesser) value than in the molecule. This is because the distance between the atoms in the activated complex is greater than in the molecule.

Note that although the energies of various activated bonds can be calculated by quantum-mechanical methods using Eqn. (19), such calculations can hardly give results which agree numerically with experiment. The approximations which form the basis of the London formula used in deriving relation (19) are too rough for such agreement.

Therefore the problem of a more correct quantum-mechanical treatment of the additivity principle and a development of methods for calculating the energy of activated bonds are extremely pressing§.

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The above-mentioned principle of the additivity of the energy of the activated complex directly connects the reactivity of different molecules and radicals with their structure. It allows a simple and graphical interpretation of the activation energy of most varied reactions to be given—including extremely complex reactions which are at present inaccessible to other theories. The additive scheme of calculation makes it possible to determine the activation energy of various chemical reactions very easily and with an accuracy sufficient for practical purposes.

This work shows that to a certain extent a formal approach to the nature of an activated complex which considers it by methods used for ordinary molecules is sufficiently well-founded, both qualitatively and quantitatively.

The purely empirical concept of an activated bond which exhibits a definite energy evidently has a very real significance.

The most important task standing now in this direction is that of defining more accurately the physical essence of the nature of the activated bond and of providing a theoretical basis for and understanding the additivity principle. This is an extremely complex quantum-mechanical problem the solution of which will facilitate to a great extent an understanding of the essence of the elementary chemical act.

§ After the manuscript of the present article had been submitted to the Editors, Szabo's paper[104] appeared, in which an attempt was made to calculate the activation energy by the equation $E = \Sigma Q_{br} - \alpha \Sigma Q_{form}$, outwardly similar to our Eqn. (8), where α is a coefficient empirically selected for each type of reaction. Unlike Eqn. (8) here the second term depends *solely* on the bonds formed. The additivity of the energy of the activated complex is not discussed in Szabo's paper.

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MODERN METHODS OF SEPARATING ZIRCONIUM AND HAFNIUM

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I. INTRODUCTION

The separation of the chemical elements zirconium and hafnium, which are encountered in nature only in the presence of one another in isomorphous crystals and whose chemical properties are extremely similar, was carried out by de Hevesy and Coster more than forty years ago[1], but the industrial application of processes for the separation of zirconium and hafnium and the production of these metals began much later, in the nineteen-fifties, in connection with the development of nuclear weapons (particularly naval weapons) and the production of nuclear energy[2]. Unlike most other fields of application of zirconium and its compounds—in ferrous and non-ferrous metallurgy, chemical plant construction, the manufacture of ceramics, refractories, glass, and enamels, industrial catalysis, etc.[2-6]—where it is possible to use zirconium without the expensive preliminary purification from hafnium, the chain reactions of nuclear fission require "reactor grade" zirconium, with the minimal possible hafnium concentration. "Reactor grade" zirconium is used chiefly in the form of alloys, as constructional material for nuclear reactors. Here use is made of the exceptionally favourable combination of properties shown by zirconium—the low effective capture cross-section for thermal neutrons, equal to 0.18 barn, compared with a figure of up to 3.5 barn for the natural mixture of zirconium and hafnium containing 1–3 wt. % of the latter, and the high mechanical strength and corrosion resistance at temperatures of up to 550°C in aggressive media.

Although the properties of hafnium and its compounds have been insufficiently studied, it is to be expected, by analogy with zirconium, that hafnium should find fairly extensive application in such fields of modern technology as electrical engineering, radio engineering, metallurgy, the optical industry, etc. The small scale of world production (several dozen tons per year) and the comparatively high cost of hafnium, however, together with the possibility of replacing it in most instances by the more readily available zirconium, has meant that up to the present most hafnium is used in nuclear technology. In contrast to zirconium, hafnium is capable of intensive absorption of thermal neutrons (capture cross-section 115 barn), and this, together with the high corrosion resistance and mechanical strength of the metal and its alloys at both low and elevated temperatures and with exposure to radiation, makes it valuable as a material for the control rods of nuclear reactors. The use of hafnium in assemblies providing protection against irradiation by thermal neutrons is also of considerable importance. The possibility of using hafnium dioxide and boride in the field of nuclear energy has recently been studied.

With increase in the scale of production and decrease in the cost, hafnium and its compounds are beginning to be used in the other branches of industry and technology noted above; the consumption of hafnium for these purposes is still relatively low, however. Extremely promising applications are the use of hafnium as constructional material for jet engines and guided missiles, in view of the ability of hafnium to absorb and give up heat more than twice as rapidly as zirconium or titanium, and also its use for alloying with refractory metals[2]. With time, hafnium will probably find application in the manufacture of chemical apparatus, and hafnium compounds may be used as catalysts. At the present time, numerous studies are being carried out to find new branches of modern technology, in which the use of hafnium might be promising. In connection with the features described above, the scale of the production of "reactor grade" zirconium and hafnium is increasing rapidly. Thus in 1950 the largest producer of these metals—the United States industry—produced 9 tons of "reactor grade" zirconium and several kilogrammes of hafnium, whereas the corresponding figures for 1959 were 1350 tons and 30 tons respectively[2].

A large number of methods for the separation of zirconium and hafnium have been proposed and tested, such as fractional crystallisation, precipitation, sublimation, distillation, or rectification; selective dechlorination of the oxides, reduction of the chlorides, or electrolysis; adsorption; ion exchange; selective liquid extraction; etc. It should, however, be noted that up to the present, even the best of the methods which are described in the literature and used in industry are comparatively complex due to the extensive difficulties associated with the problem of separating elements whose properties are so similar†.

Several fairly extensive reviews have been devoted to the problems of separating zirconium and hafnium, but one of the most complete Soviet reviews[7] appeared more than ten years ago and is naturally somewhat out of date. Works

† The similarity in the properties of zirconium and hafnium is due to the similarity in their atomic dimensions (the atomic radii are R_{Zr} = 1.45 Å and R_{Hf} = 1.44 Å) and the similarity in the configuration of the valency electrons ($4d^2 5s^2$ for zirconium and $5d^2 6s^2$ for hafnium)[4].

by foreign authors[5,6,8-11] say little about results obtained by Soviet research workers, so that it has become necessary to compile a new review containing information on the present state of this problem in the Soviet Union and abroad.

Modern technology, for the industrial separation of mixtures of zirconium and hafnium, uses chiefly the methods of liquid extraction, and also in some instances the methods of cation exchange and fractional crystallisation of potassium fluorozirconates and fluorohafnates. In the present review, most attention is paid to these methods, particularly the extraction method. The description of many other methods, chiefly older versions of methods for separating zirconium and hafnium, is omitted. This material can be found elsewhere[5-10], together with bibliographies of the original papers on these methods. In view of the extensive nature of the topic and space restrictions, the present paper gives only the fundamental principles and a brief description of the technological processes for the separation of zirconium and hafnium. More detailed information on the theory of these processes is given in a number of monographs and original papers, to which reference is made at appropriate points in the text. General information on the present state of the chemistry of aqueous solutions of zirconium and hafnium, necessary for an understanding of the hydrometallurgical processes involved in the separation of these elements, together with bibliographies, can also be found elsewhere[12-15].

II. METHODS FOR SEPARATING ZIRCONIUM AND HAFNIUM

1. Fractional Crystallisation

This method of separation makes use of comparatively small differences in the solubilities of individual compounds of zirconium and hafnium[4-6,11]: the oxide chlorides or oxide bromides, citrates, acetylacetonates, and the double oxalates, sulphates, or fluorides with ammonium or potassium. The efficiency of separation by fractional crystallisation is therefore low. Systems containing the double fluorides (fluorozirconates or fluorohafnates) of potassium or ammonium were the first to be used for the separation of zirconium and hafnium, and these methods, as noted above, have to some extent retained their importance to the present day.

In the fractional crystallisation of the double fluorides (fluorozirconates and fluorohafnates) of potassium or ammonium, the hafnium salts, which are more soluble than the zirconium salts, concentrate in the mother-liquors, and the zirconium in the crystals is gradually purified from hafnium. Several hundred recrystallisations are required in order to obtain pure hafnium from the usual raw material. On the other hand, modern versions of this method make it possible to obtain a "reactor grade" zirconium salt, containing not more than 0.05% hafnium impurity, in a much smaller number of recrystallisations (12–18). Thus this method, despite the simplicity of the individual crystallisations, is now used only for the preparation of "reactor grade" zirconium.

In a version of the method developed in the Soviet Union by Sazhin and Pepelyaeva[16] for the preparation of "reactor grade" zirconium dioxide and hafnium concentrates by recrystallising the fluorozirconates and fluorohafnates, the finely ground zirconium concentrate is sintered with potassium fluorosilicate at 650–700°C to give a sinter of potassium fluorozirconate and fluorohafnate with silicon dioxide. The sinter is finely ground, the fluorozirconate and fluorohafnate are leached out with dilute hydrochloric acid at 85°C, and the extract is left to stand. Cooling of the clarified solution gives crystals of K_2ZrF_6 containing 1.5–2.5% K_2HfF_6; the crystals are compressed, washed with water, and subjected to fractional crystallisation. This is carried out using a countercurrent scheme with 16–18 stages; the hafnium is concentrated in the mother-liquors, and the zirconium in the crystals. The original potassium fluorozirconate crystals containing hafnium impurity are passed to the first stage of the crystallisation and are successively recrystallised from mother-liquors containing an ever-decreasing percentage of hafnium impurity. The crystals are dissolved at 80–90°C, and recrystallise on cooling. In the last two stages, distilled water is used for the dissolution. The mother-liquors from the first and second stages are removed from the crystallisation cycle; precipitation with ammonia from these mother-liquors gives a 6% hafnium concentrate, which is taken for subsequent enrichment by extraction or ion exchange. The final K_2ZrF_6 crystals contain down to 0.01% K_2HfF_6. Similar processes for the separation of zirconium and hafnium were tested by Kawecki[17] in the USA and by the Knaaks[18] in the German Democratic Republic. The development of the theory of these processes is still continuing. Recently, Egerev and coworkers[19] published new data obtained in physicochemical studies of the K_2ZrF_6–K_2HfF_6–H_2O system by the solubility method; these data give more complete information on the regular features of the processes involved in the separation of zirconium and hafnium by fractional crystallisation of potassium fluorozirconates and fluorohafnates.

A new version of the method of fractional crystallisation was recently patented in Japan[20]. Dissolution of pyridinium chlorozirconate in chlorine water at 60°C with subsequent cooling and separation of the resulting crystals increases the hafnium concentration (calculated on the sum Zr + Hf) by a factor of 3 compared with the original concentration.

2. Fractional Precipitation

Methods for separating zirconium and hafnium by fractional precipitation for the most part make use of differences in the solubilities of compounds of these elements, and also of differences in the stabilities of their complexes. In the large number of versions of these methods[4-11], studies have been made of separation by organic compounds (benzoic, tartaric, salicylic, and mandelic acids, and their derivatives) and by inorganic compounds—phosphoric acid, sodium hexacyanoferrate(II), hydrogen peroxide, ammonia, etc. The results of studies carried out over many years have shown that the methods of fractional precipitation are tedious and that the separation process is time-consuming; the degree of enrichment achieved in one stage of the fractionation is comparatively small. Thus even the most effective of these methods—certain versions of the phosphate and hexacyanoferrate(II) methods—are not now used in large-scale industrial production, although under certain conditions they can still be used in preparative laboratory work for the separation of zirconium and hafnium. Some versions of the phosphate and hexacyanoferrate(II) methods of separation are described below.

Phosphate method. (a) In Larsen's method[21], a 2–5% solution of phosphoric acid in 10% sulphuric acid, and a 2–5%—calculated as $(Zr, Hf)O_2$—solution of zirconium and hafnium sulphate in the same acid are added from spray jets with constant stirring to a 10% solution of sulphuric acid at 70–75°C. This gives a compact phosphate precipitate which settles readily, and in which the hafnium is concentrated. The precipitate is filtered off and washed with water. The resulting liquid paste is cooled with ice and treated with a cold solution of sodium hydroxide and sodium peroxide. The mixture is heated at 50–70°C until all the zirconium and hafnium is precipitated as the hydrated peroxides of these elements. The precipitate is filtered from the sodium phosphate solution and dissolved in sulphuric acid, and a new cycle of the phosphate precipitation is carried out. After seven successive cycles of this process, with precipitation of 55% of the total $(Zr, Hf)O_2$ from solution in each cycle, the concentration of HfO_2 in the concentrates is increased by a factor of more than 7, from 13% to 93%. With raw material containing 2–3% HfO_2, zirconium dioxide almost free from hafnium is left in the mother-liquor after two successive fractional precipitations of the phosphates from solution.

(b) In Peters' method[22], the zirconium and hafnium hydroxides are dissolved with heating in dilute (1 : 3) hydrochloric acid, and the resulting solution is treated with $NH_4H_2PO_4$ solution at 40°C. The resulting precipitate of zirconium and hafnium phosphates is washed with distilled water to remove phosphate ion, and dissolved with stirring in 10% oxalic acid solution at room temperature. The resulting solution is heated to 40–60°C and treated with a quantity of oxalic acid equal to that used for the dissolution. The solution is then heated on the water-bath at 40–60°C for a prolonged period varying from several days to several weeks. This is necessary for "aging"—the formation of a stable oxalato-complex of zirconium and hafnium. This complex is then subjected to fractional decomposition by the dropwise addition, with stirring at 70°C, of a solution of the precipitant—a mixture of hydrochloric acid and a solution of ammonium oxalate saturated in the cold. After some time an opalescence appears; this is eliminated by adding ammonium oxalate solution, after which the addition of the precipitant solution is continued until a turbidity appears. The addition of the precipitant is then stopped and the solution is stirred for a further 2 h. To increase the efficiency of the separation of zirconium and hafnium, a "seed" consisting of a fine crystalline nucleus of freshly-precipitated hafnium phosphate is added to the solution before the start of crystallisation. The resulting precipitate is separated from the mother-liquor, filtered, washed, and dissolved in 10% oxalic acid, from which the zirconium and hafnium hydroxide is precipitated.

The degree of separation of zirconium and hafnium by this method, when the "aging" of the complex is effective, is fairly high: from ~ 9% hafnium concentrates the first fraction gave 85% concentrates, and the sixth or seventh fractions gave zirconium dioxide containing down to 0.01% HfO_2. The chief disadvantage of the method is the time required for "aging" of the oxalato-complex.

The hexacyanoferrate(II) method. In the fractional precipitation of zirconium and hafnium hexacyanoferrate(II) from acid solutions of their mixtures in the presence of complex-forming reagents, hafnium is concentrated in the precipitate, since its hexacyanoferrate(II) complexes are less stable and less soluble than the zirconium complexes. The compositions of zirconium and hafnium hexacyanoferrates(II) were studied by Ionova and Tananaev[23], Savenko and Sheka[24], and others; the compositions depend on the conditions of preparation.

In Prandtl's method[25], freshly precipitated zirconium and hafnium hydroxides are dissolved in dilute sulphuric acid, the solution is boiled, and treated with ammonium sulphate and a solution of oxalic acid, saturated in the cold. The resulting solution, containing zirconium and hafnium in the form of anionic complexes, for example, $[ZrO(SO_4)_2]^{2-}$ and $[HfO(SO_4)_2]^{2-}$, is treated with sufficient sodium hexacyanoferrate(II) solution to give partial precipitation of zirconium and hafnium hexacyanoferrates(II). The precipitation is carried out at room temperature (according to Aleksandrov and coworkers[26], it is better to carry out the precipitation at 60°C). The hexacyanoferrate(II) precipitate, which is enriched in hafnium, is left to stand for a prolonged period and then separated from the solution; treatment with hot NaOH solution is then carried out to precipitate zirconium and hafnium hydroxides. These are washed with hot water, dissolved in dilute sulphuric acid, and passed to the next stage of the hexacyanoferrate(II) concentration of hafnium. According to Prandtl, 1% raw material after 6 precipitation cycles gives 95% hafnium concentrates.

Although stable results on the separation of zirconium and hafnium were not achieved in Prandtl's experiments, the higher efficiency of the hexacyanoferrate(II) process compared with most other processes based on fractional precipitation led to further studies of this method. Schumb and Pittman[27] put forward a slightly modified version of the hexacyanoferrate(II) process, the chief difference being that the precipitation of the hexacyanoferrates(II) is carried out from a solution of zirconium and hafnium oxide chlorides to which concentrated sulphuric acid has been added (the other components of the reaction mixture are the same as those in Prandtl's version). The sodium hexacyanoferrate(II) solution is added even more slowly—dropwise; the hexacyanoferrate(II) precipitates are filtered off and decomposed not with NaOH but with ammonia. When this version of the hexacyanoferrate(II) method is used, a 12% hafnium concentrate gives an 80% concentrate after four precipitation cycles.

Thus the hexacyanoferrate(II) method makes it possible, after a comparatively small number of fractional precipitations, to obtain high-percentage hafnium concentrates. One specific disadvantage of this method is that partial decomposition of sodium hexacyanoferrate(II) by sulphuric acid during the hexacyanoferrate(II) precipitation leads to the liberation of HCN vapour into the atmosphere, so that the process must be carried out with efficient ventilation, and also to contamination of the precipitates with iron.

3. Fractional Distillation

This method of separation is based on the use of the difference in the boiling points of various zirconium and hafnium compounds. Earlier, tests were carried out on methods for separating these elements by sublimation of their tetrafluorides and tetrachlorides[28] or by distillation of the tetrafluorides from solution in molten potassium fluorozirconate and fluorohafnate[28], or of the tetrachlorides at an elevated pressure of ~ 10 atm.[29] Although the efficiency of these methods was found to be comparatively low, the idea of using sublimation to separate zirconium

and hafnium has not been abandoned completely: comparatively recently, a sublimation separating apparatus of the column type was patented [30].

More effective methods of separation are those based on fractional distillation of complex compounds—products of the reaction of zirconium and hafnium tetrachlorides with phosphorus(V) chloride and, more particularly, phosphoryl(V) chloride. The compositions of the zirconium complexes are as follows—with PCl_5: $ZrCl_4.PCl_5$ and $2ZrCl_4.PCl_5$ [31,32]; and with $POCl_3$: $ZrCl_4.2POCl_3$, $ZrCl_4.POCl_3$ [33,34], and $2ZrCl_4.POCl_3$. [31] The compositions of the hafnium complexes are analogous to those of the zirconium complexes, for example: $HfCl_4.2POCl_3$ and $HfCl_4.POCl_3$ [34,35]. It has also been suggested [36] that the products of the reaction with $POCl_3$ are not individual chemical compounds, but only azeotropic mixtures.

Although the difference in the boiling points of the complexes formed by phosphoryl(V) chloride with zirconium and hafnium tetrachlorides is comparatively small (360° and 355°C respectively) [31], effective separation of zirconium and hafnium can be achieved when the number of plates in the fractionating column is sufficiently large. Litton [37] carried out the fractional distillation of a mixture of commercial zirconium tetrachloride and phosphoryl(V) chloride in columns, each containing 50 plates; the hafnium concentrated in the distillate. Four successive fractional distillation cycles gave concentrates containing 98.5% HfO_2 in $(Zr, HF)O_2$, with a direct yield of hafnium equal to 25%. The concentration of HfO_2 in the residues in the still, calculated on the total $(Zr, Hf)O_2$, was 1.5–2%. The final distillate was dissolved in methanol, and hafnium hydroxide was precipitated with ammonia. The method involving fractional distillation of the complex compounds (or mixtures) of zirconium and hafnium tetrachlorides with phosphorus chlorides has now been fairly well studied. Thus Nisel'son [38], in one column with 50 plates, obtained zirconium containing less than 0.05% hafnium from a starting material in which the concentration was 1%; the yield of zirconium amounted to ~ 40%.

It has been reported [6] that an assembly has been planned for separating zirconium and hafnium by this method, with a continuously operating packed column of stainless steel, capable of an annual production of 18 tons of metallic zirconium containing less than 0.1% hafnium.

Ogburn and Fischer [39], using a high-efficiency glass apparatus, obtained zirconium containing ~ 0.01% hafnium from an original concentrate containing 3% hafnium.

The study of the possibility of separating mixtures of zirconium and hafnium tetrachlorides without the addition of phosphorus compounds is also of considerable interest. A satisfactory solution of this problem would make it possible to use the products of the separation of zirconium and hafnium for direct conversion into the metals. Thus in recent years, papers on the separation of zirconium and hafnium tetrachlorides by fractional distillation under pressure [40-42] or by extractive fractional distillation [40,43,44] have again appeared, at a higher technical level than earlier papers.

Extractive fractional distillation is carried out in columns irrigated with melts in which $ZrCl_4$ and $HfCl_4$ are readily soluble (NaCl, KCl, $SnCl_2$, $ZnCl_2$, etc., and their mixtures). The vapour in the upper part of the columns is enriched in hafnium; zirconium is concentrated in the melt leaving the section of the column adjoining the still. The temperature conditions for some systems are as follows: 350–500°C in the lower section of the columns and 330–350°C in the upper section (melt of NaCl and KCl); 470°C in the lower section of the columns and 250–450°C in the upper section of the columns ($SnCl_2$ melt). The efficiency of extractive fractional distillation is still comparatively low, however. For example, for an $SnCl_2$ melt, the separation factor in the column is only 2.

Laboratory experiments on fractional distillation under pressure have been carried out at 20–30 atm [31] at temperatures of ~ 450°C in the rectifying section of the columns; under these conditions the $ZrCl_4$ and $HfCl_4$ in the column are present partly in the liquid state and partly in the vapour state‡. The properties of gaseous and liquid zirconium and hafnium tetrachlorides have been studied [41,42]. The fractional distillation of a mixture of zirconium and hafnium tetrachlorides containing ~ 0.3% $HfCl_4$ gave 69–88% $ZrCl_4$ containing less than 0.03% hafnium, together with 7–11% hafnium concentrates in the first distillate fraction. In large-scale experiments in a column with metal packing [45], fractional distillation of mixtures of zirconium and hafnium tetrachlorides with an initial $HfCl_4$ concentration of ~ 1.5–2.5% gave zirconium containing less than 0.05% hafnium, in yields of more than 50%.

Advantages of the fractional distillation method for separating zirconium and hafnium are the comparatively high capacity of the apparatus and the possibility of achieving extensive purification of the products and establishing a continuous process. The introduction of this method in industry, however, particularly the version involving fractional distillation under pressure, first requires the solution of a number of complex problems, associated chiefly with the development of apparatus for carrying out the process—the selection of materials resistant to aggressive media at high temperatures and pressures, the design of fairly complex apparatus, etc.

4. Selective Dechlorination of Zirconium Tetrachloride

Thermodynamic calculations [46,47], carried out for the conversion of zirconium and hafnium tetrachlorides into the corresponding oxides by reaction with oxygen according to the equations

$$ZrCl_{4\,(gas)} + O_2 \rightleftarrows ZrO_2 + 2\,Cl_2$$

$$HfCl_{4\,(gas)} + O_2 \rightleftarrows HfO_2 + 2\,Cl_2$$

showed that the conversion of zirconium tetrachloride into the dioxide is possible, whereas the analogous process for hafnium tetrachloride is almost unrealisable. On this basis, Prakash and Sundaram [47] proposed a method for separating zirconium and hafnium by the selective dechlorination of zirconium tetrachloride with oxygen. A mixture of zirconium and hafnium tetrachlorides containing 2.54% HfO_2 in $(Zr, Hf)O_2$, previously purified from traces of silicon, iron, and titanium, was placed in a tubular quartz furnace from which it was sublimed at 300–325°C and carried by a stream of dry chlorine into the upper part of a vertical tubular furnace, into which a mixture of dry chlorine and oxygen was also passed. The mixture of gases entered the furnace from above; the white zirconium dioxide powder formed in the reaction was deposited in a collector connected to the foot of the reaction tube in the

‡ At atmospheric pressure, however, the sublimation temperatures of $ZrCl_4$ and $HfCl_4$ (335° and 314°C) are lower than the melting points (434° and 432°C respectively), and there is no need for rectification of the liquid phase.

furnace. The gas mixture passed into a condenser, where the unreacted chlorides—the hafnium concentrates—were deposited. At a chlorine: oxygen ratio of 1 : 1, a temperature of 500°C, and a duration of reaction equal to 2 h, the concentration of HfO_2 in the zirconium oxide deposited was 1.29% (half of the initial value) and the yield of zirconium oxide 90–97%; the volatile fraction contained more than 25% HfO_2.

It was thus shown possible to achieve partial separation of zirconium and hafnium in a single cycle by this method; a tenfold enrichment of the hafnium concentrates was achieved, but the purification of zirconium from hafnium was much less efficient.

Koemon Funaki and Kotaro Uchimura[48] studied the kinetics of the dechlorination of zirconium and hafnium tetrachlorides by oxygen. Their experiments confirmed that selective dechlorination of $ZrCl_4$ takes place. Contrary to the views previously expressed[46,47], however, these authors state that appreciable dechlorination of $HfCl_4$ also takes place, reducing the efficiency of the separation.

Later, it was suggested[49] that the selective dehalogenation be carried out in a continuously operating apparatus, preferably using zirconium and hafnium tetrachlorides as starting materials; the tetrabromides and tetraiodides can also be used. The process was carried out at 500–900°C, which is higher than the temperature in the first version of the method.

5. Selective Reduction of the Tetrachlorides by Metals

Although methods for the reduction of zirconium halides by aluminium and zirconium were developed fairly early[50–53], it was only some years later that research workers turned their attention to the marked difference in the abilities of $ZrCl_4$ and $HfCl_4$ to undergo reduction[54–57]. This indicated the possibility of using selective reduction of the tetrachlorides to separate zirconium and hafnium. This process was first developed by Newnham[55,56]; the original mixture of (Zr, Hf)Cl_4 containing 1.5% HfO_2 in (Zr, Hf)O_2 was reduced with zirconium in an evacuated vessel at 300–550°C. $ZrCl_4$ was reduced to $ZrCl_3$; the extent of the reduction of $HfCl_4$ was several times smaller. The hafnium tetrachloride and unreduced zirconium tetrachloride were sublimed off. A reduction temperature of 420°C and a duration of reaction equal to 8 h gave the sublimate with highest hafnium content—5.7%. It was found that the rate of reduction decreases considerably due to the formation of a sinter of the trichloride and unreacted zirconium powder. The reaction vessels were therefore subjected to repeated intensive agitation during the reduction; it was found that for the above temperature and duration of the process, this increased the concentration of hafnium in the sublimate to 29.4%, with a 95% yield of this element. The concentrates obtained were converted into hafnium dioxide by ion exchange or liquid extraction. The degree of reduction of $ZrCl_4$ to $ZrCl_3$ also amounted to 95%; the concentration of hafnium in the latter was reduced to 0.05%. The zirconium trichloride obtained was heated in a vacuum; disproportionation took place according to the reactions

$$2\,ZrCl_3 \rightleftarrows ZrCl_2 + ZrCl_4$$

$$2\,ZrCl_2 \rightleftarrows Zr + ZrCl_4.$$

A temperature of 540°C was found to be sufficient for complete disproportionation of $ZrCl_3$, but the disproportionation of the dichloride is more difficult. The $ZrCl_4$ was distilled off, and the $ZrCl_2$ was used as reducing agent in subsequent cycles.

A disadvantage of the reduction by zirconium is that $ZrCl_3$ begins to disproportionate even at 300°C, as a result of which the $HfCl_4$ being sublimed off is diluted with unreduced $ZrCl_4$. This disadvantage is eliminated if the reduction is carried out with aluminium powder at 300°C.[55] Moreover, at this temperature a melt of $ZrCl_3$ in $AlCl_3$ is obtained, and this prevents the formation of a sinter. Versions of this method, in general differing little from one another, were patented in several countries. The starting materials were (Zr, Hf)Cl_4 [58–61] or (Zr, Hf)I_4 [62,63] mixtures.

In the Soviet Union, the separation of zirconium and hafnium by selective reduction of their tetrachlorides was studied under laboratory conditions by Emel'yanov and coworkers[64,65], by Kozhemyakin and coworkers[66,67], and by others. The thermodynamic principles and kinetics of the process were studied, and the optimal conditions for carrying it out were determined. The results of the studies made it possible to develop a laboratory method for separating zirconium and hafnium. Using this method, it is possible to reduce the concentration of hafnium in (Zr, Hf)Cl_4 from 1–1.5% to 0.05% in one cycle, but the degree of reduction is comparatively low—not more than 70–75%; the concentration of hafnium in the concentrates obtained reaches 3–4%. With further increase in the degree of reduction, the concentration of hafnium in the purified $ZrCl_4$ and the hafnium concentrates increases; thus for 99% reduction of zirconium, the $ZrCl_4$ obtained contains 0.3–0.5% HfO_2, and the concentrates contain 25–29% HfO_2 (calculated on the total oxides).

Thus this method is of undoubted interest for further studies, particularly since its further development might make it possible to eliminate completely the hydrometallurgical processes of converting the (Zr, Hf)Cl_4, obtained by the chlorination of zirconium, into pure $ZrCl_4$ and $HfCl_4$, and then into the corresponding metals.

6. Electrolysis of Melts

After it had been shown, in the nineteen-twenties, that methods for separating zirconium and hafnium, based on the small difference in the mobilities of the ions of the two metals, had a low efficiency[68,69], the electrolysis method was not tested further for this purpose for a long time. It was only when the industrial production of zirconium by electrolysis was successfully developed that the attention of research workers was again drawn to this problem. The possibilities provided by the electrolytic separation of zirconium and hafnium can be illustrated by a recent paper devoted to the study of this problem[70]. The electrolysis vessel contained a mixture of 65% NaCl and 35% K_2ZrF_6. The electrolysis was carried out at 850°C in an atmosphere of argon previously purified from traces of nitrogen and oxygen. The initial current density at the cathode was 2 A cm^{-2}; the current strength was 10 A, and the potential difference 5 V. The graphite crucible in which the melt was placed was used as the anode, and the cathode consisted of rods of heat-treated molybdenum, nickel, and low-carbon steel. Metallic zirconium powder containing 0.05% hafnium was obtained in one cycle from fluorozirconate containing 0.6% hafnium. When the duration of electrolysis exceeded 2 h, the degree of separation began to decrease sharply; within this period, 40% of the metal taken was extracted. It was possible to extract a further 25% of the metal in additional cycles.

Smirnov and coworkers[71] showed that an even greater degree of purification of zirconium from hafnium can be achieved by the electrolysis of K_2ZrF_6 in an NaCl–KCl melt. The concentration of hafnium in zirconium is decreased by a factor of 20 at 700°C and by a factor of 70 at 650°C. The hafnium is concentrated in the electrolyte.

Although the efficiency of electrolysis as an independent method for the separation of zirconium and hafnium is comparatively low, the results obtained indicate the possibility of additional incidental purification of reactor zirconium during its industrial preparation by electrolysis.

Electrolytic refining in NaCl–KCl or LiCl–KCl melts can also be used to purify $HfCl_4$ from traces of iron, aluminium, etc.[72]

7. Adsorption and Ion Exchange

Sorption (chromatographic) methods for separating zirconium and hafnium are based on differences in the behaviour of these elements in molecular or ionic forms in processes of sorption or desorption on adsorbents or ion-exchange resins. The general theoretical principles of these processes are given in many papers and monographs[73,74].

(a) Partition chromatography. In the original version of this method[75,76], a cellulose mass impregnated with aqueous zirconium nitrate solution was treated with an eluant consisting of a mixture of diethyl ether and nitric acid (7 : 1). As a result of the difference in the constants for distribution between the aqueous and organic phases, zirconium was eluted more rapidly than hafnium. The degree of extraction of purified zirconium, containing less than 0.01% HfO_2, amounted to ~ 70%; the hafnium was concentrated in the last fractions. In a method developed by Chou and Tao[77] for the separation of zirconium and hafnium by paper chromatography, the combustible and explosive diethyl ether was replaced by less dangerous eluants consisting of mixtures of tributyl phosphate (TBP) with butanol and xylene (or benzene) in 8–10 M HNO_3. The authors reported complete separation of zirconium and hafnium.

Data on the separation of these elements by reversed-phase chromatography were published recently. Crawley[78] passed a solution of zirconium and hafnium in an eluant consisting of a mixture of 25% HNO_3 and 50% NH_4NO_3 through a column containing kieselguhr and TBP; up to 88% hafnium passed into the eluate. Better results were obtained by Fritz and Frazee[79], who used a stationary phase consisting of polytetrafluoroethylene (Teflon-6) treated with isobutyl methyl ketone previously brought into equilibrium with 3 M HSCN solution. A hydrochloric acid solution of the mixture of zirconium and hafnium was mixed with the eluant and placed in the upper part of the column, after which the zirconium was eluted with an aqueous solution of a mixture of NH_4SCN and $(NH_4)_2SO_4$. The hafnium was then eluted with a solution of $(NH_4)_2SO_4$ or H_2SO_4. Quantitative separation of zirconium and hafnium was achieved.

The methods of partition chromatography described above are unsuitable for industrial use. These methods, however, particularly those involving reversed-phase chromatography, can apparently be used for the laboratory preparation of small quantities of pure zirconium and hafnium, and for the analytical determination of the concentrations of these elements in their mixtures.

(b) Adsorption on silica gel. Methods for separating zirconium and hafnium on silica gel are based on differences in the degree of adsorption and desorption of various compounds of these elements. A recent paper[80] described a study of the mechanism of the sorption of zirconium from nitric acid medium on silica gel; the kinetics of sorption are determined by the rate of diffusion. There are no data indicating that the separation of zirconium and hafnium may take place by an ion-exchange mechanism (as has been shown for the sorption of various metals on silica gel[81]).

Work on the separation of zirconium and hafnium on silica gel was first published by Hansen and coworkers[82,83], and later by Beyer and coworkers[84]. In Beyer's method, a 20% methanol solution of $ZrCl_4$ containing 2–2.5% $HfCl_4$ was passed through a column of silica gel previously activated at 300°C. Hafnium was selectively sorbed by the silica gel, as a result of which the concentration of hafnium in the zirconium in the solutions leaving the column was reduced to ~ 0.3%. Subsequent elution with a 1.9–2.5 *N* solution of HCl in methanol also eluted chiefly zirconium. 7 *N* sulphuric acid was then passed through the column to elute the enriched hafnium concentrate. This was converted into the tetrachloride and the cycle was repeated. Two cycles of this process gave a 90% hafnium concentrate with a yield of hafnium equal to ~ 70%; pure hafnium was not obtained.

Zirconium and hafnium were also separated from solutions of their oxide chlorides in methanol by a frontal chromatographic process on silica gel[85]. From the original 3–15% hafnium concentrates the authors obtained purified zirconium dioxide containing ≤ 0.01% HfO_2, with a yield of zirconium equal to 70–75% of the original quantity (~ 0.23 kg ZrO_2 per kg silica gel) and hafnium concentrates containing more than 20% HfO_2.

The method of separation by adsorption was also tested in continuously operating columns[86]; zirconium dioxide containing only 0.01% HfO_2 was obtained from a raw material containing 2% HfO_2. On the basis of these results, a pilot-plant separating assembly was designed, capable of an annual production of 5 tons of zirconium, purified to a hafnium content of less than 0.01%.

In subsequent studies it was found possible to obtain higher degrees of separation under optimal laboratory conditions by altering the method of preparing the silica gel. Thus Koemon Funaki and coworkers[87] used silica gel, treated with alkali solution, to purify zirconium from hafnium. Waltenberger-Raźniewska[88] obtained an 80% yield of purified zirconium dioxide (HfO_2 content ≤ 0.01%) by using silica gel obtained by neutralising Na_2SiO_3 solution with hydrochloric acid in the presence of a considerable quantity of $Ni(NO_3)_2$.

c. Cation exchange. The differences in the stabilities of zirconium complexes and the corresponding hafnium compounds in sulphuric and certain other acids have been used successfully to separate these elements on cation-exchange resins. The first paper on the separation of zirconium and hafnium by cation exchange appeared in 1948.[89] Finely divided Dowex-50 resin—a polystyrene resin with active sulphonic acid groups—was treated with a solution of zirconium and hafnium oxide chlorides in 2 M perchloric acid; at this acidity, zirconium is present in solution chiefly in cationic form[90-92]; recently, the same has been proved for hafnium. About 80% of each metal was sorbed by the resin, which was then transferred to the

upper part of a column of the same resin (without metal) and eluted with 6 *N* hydrochloric acid. 99.9% HfO_2 was isolated from the first fraction of eluate in 66% yield relative to the original quantity. In this first work, milligramme quantities of zirconium and hafnium were used; Newnham[93], however, used this method to separate several grammes of the mixture. The yield of 99.9% HfO_2 amounted to only 42%.

Several versions of the cation-exchange process for separating zirconium and hafnium were subsequently developed in a series of papers by Lister and coworkers[94-97]. The efficiency of desorption by hydrochloric, perchloric, nitric, oxalic, and sulphuric acids was first studied; best results were obtained using sulphuric acid. Later, Benedict and coworkers[98] showed that a mixture of dilute nitric and citric acids is an effective desorbent, but sulphuric acid is much cheaper and is therefore more promising for preparative and particularly industrial use. The separation of zirconium and hafnium on desorption by sulphuric acid is due chiefly to the marked difference in the stabilities of the sulphato-complexes of hafnium and zirconium in solution. Thus according to Ryabchikov and coworkers[99,100], the stability of the sulphato-complexes of zirconium in solution under certain conditions is three times that of the hafnium complexes. Almost no separation of zirconium and hafnium takes place during sorption on cation-exchange resins from nitric acid solutions. This was confirmed by a study of the isotherms and kinetics of the cation-exchange sorption on the strongly acidic KU-2 sulphonic acid cation-exchange resin§ produced in the Soviet Union[101,102].

In Lister's method, to obtain zirconium purified from hafnium from a raw material containing 20% HfO_2 in $(Zr, Hf)O_2$, the original 0.01 M solution of zirconium oxide chloride in 2 *N* hydrochloric, nitric, or perchloric acid was passed through a column of Dowex-50 or Zeocarb-225 cation-exchange resin. 0.8–1.2 *N* H_2SO_4 was used for the subsequent elution. The first fraction contained 98–99% of the original quantity of zirconium, containing 0.01% hafnium. The hafnium remaining in the column was extracted with 0.05 *N* hydrofluoric or oxalic acid.

In another version of the method, the sorption of zirconium and hafnium was carried out from 0.8–1.2 *N* H_2SO_4 solution. Zirconium containing less than 0.05% hafnium was obtained from the first fractions of eluate. The separation of hafnium from zirconium on Wofatit[103] was found to be less efficient.

Lister also tested a semicontinuous separation process in a battery of two columns. A 0.01 M solution of zirconium nitrate in 2 *N* HNO_3 was passed through the first column, after which 0.8–1.5 *N* H_2SO_4 was passed successively through both columns. Up to 90% of the sorbed zirconium and less than 0.05% of the hafnium was extracted in the first fraction. Hafnium was then extracted by dilute hydrofluoric or oxalic acid in good yield, in the form of a high-percentage concentrate.

Other papers describe various versions of the cation-exchange method—separations on KU-2 resin using various mixtures as eluants: 0.025 M citric acid and 1 M perchloric or nitric acid[99], or hydrochloric acid containing organic solvents (acetone, isopropyl alcohol, ethyl methyl ketone, diethyl ketone, and acetylecetone[104]); separations by Lister's method have also been carried out using ion-exchange membranes[105]. Laskorin and coworkers[106] developed a new version of the ion-exchange process using the KU-2 sulphonic acid cation-exchange resin produced in the Soviet Union; the separation factors for zirconium and hafnium reached values of 5. The original sulphuric acid solutions contained 20–30 g litre^{-1} $(Zr, Hf)O_2$ and 0.65–0.75 M H_2SO_4; fluoride ions were added to the solution to give a ratio F: Zr = 0.7–1.0. When this solution was passed through a layer of KU-2 resin, as a result of the marked difference in the stabilities of the fluorosulphato-complexes of zirconium and hafnium, the hafnium and part of the zirconium were sorbed by the cation-exchange resin, and the remainder of the zirconium was left in the solution leaving the column. The elution was carried out with 0.65 M sulphuric acid. Zirconium hydroxide containing 0.01–0.08% HfO_2 in $(Zr, Hf)O_2$ was isolated from the first fraction of the eluate, and the second fraction gave a mixture of zirconium and hafnium, which was returned to a new separation cycle. The third fraction, containing hafnium, was passed through a column of RF phosphate cation exchanger¶; the hafnium was sorbed, and the dilute sulphuric acid solution was used for elution in a new ion-exchange cycle. The hafnium was washed from the RF exchanger with ammonium oxalate solution, from which hafnium hydroxide containing 99% HfO_2 in $(Hf, Zr)O_2$ was precipitated with ammonia. Further studies of the fluorosulphate process were carried out by Pepelyaeva and coworkers[107]. An advantage of this method over other ion-exchange methods is that partial separation of hafnium from zirconium also takes place in the ion-exchange sorption process; this makes it possible to increase considerably the capacity of the ion-exchange columns.

Laskorin and coworkers[108,109] also studied the separation of zirconium and hafnium in a moving layer of ion-exchange resin, in a continuously operating countercurrent chromatographic column. The cation-exchange resin with particle size 20–50 mesh moves down the column, and the original solution and eluant solutions move up the column. The cation-exchange resin suspension is moved from the lower to the upper sections of the column by means of an airlift. The concentrations of the original solution and the eluant solution (for the desorption of hafnium), because of subsequent dilution in the column, are greater than those for the batch process; the original solution contained 65 g litre^{-1} $(Zr, Hf)O_2$ and had a total acidity of 150 g litre^{-1}; 0.8–0.9 M H_2SO_4 was used as desorbent solution. Hafnium containing down to 1% zirconium passed to the lower section of the column, and zirconium containing less than 0.03% hafnium moved into the upper section. According to the authors, the capacity of the columns in the continuous countercurrent process is three times that for the batch process.

(d) Anion exchange. At sufficiently high concentrations of hydrofluoric acid, zirconium and hafnium form anionic complexes with different stabilities. This has provided the starting point for the development of most methods for separating these elements by anion exchange. Kraus and Moore[110] sorbed zirconium and hafnium from solutions of a mixture of fluorozirconates and fluorohafnates on the strongly basic resin Dowex-1; on elution with a mixture of acids (1 M HCl + 0.5 M HF) at a rate of flow

§ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

¶ RF is a strongly acid cation-exchange resin with $-PO_3H_2$ functional groups (Ed. of Translation).

of eluant equal to 0.3 ml cm^{-2} min^{-1}, zirconium was concentrated in the first fractions, and more than 95% of the hafnium was concentrated in the last fractions. Better results were obtained by Huffman and Lilly[111] using Amberlite IRA-400 resin in the chloride form, at lower concentrations of eluant (0.2 M HCl + 0.01 M HF): the yield of purified zirconium was 70%, and that of purified hafnium containing 0.03% zirconium was 83%. Forsling[112], who studied the optimal conditions for the purification of zirconium from hafnium by anion exchange, achieved even better results on Amberlite IRA-400 resin by eluting with a mixture of 0.00008 M HF and 0.22 M HCl at a rate of flow equal to 0.04–0.15 ml cm^{-2} min^{-1}; the degree of extraction of purified zirconium amounted to 98%.

A number of papers describe the use of dilute sulphuric acid as desorbent. According to the data of Rajan and Gupta[113-115], who used finely divided Amberlite IRA-400 resin in the chloride form, the degree of extraction of zirconium dioxide purified from hafnium amounted to 94%, and the yield of spectroscopically pure hafnium amounted to 75%; the use of Dowex-2 resin gave 91.2% zirconium and 75% hafnium with the same purity; thus the efficiency of separation was approximately the same for these resins. Slightly less satisfactory results were obtained when resin fractions with a larger particle size were used. When hafnium concentrates were sorbed in a column of Amberlite IRA-400 resin in the SO_4^{2-} form and subsequently eluted with dilute sulphuric acid with varying concentration (first 0.25–0.5 N H_2SO_4 and then 3 N H_2SO_4), purified hafnium (less than 0.1% zirconium) was eluted first, followed by purified zirconium. The yield of purified hafnium was 93–95%. Huré and coworkers[116,117] also achieved effective separation of zirconium and hafnium from sulphate solutions using Dowex-2 and Amberlite IRA-400 resins, and also using Dowex-1 resin[118].

Yagodin and Orlov[119], using the weakly basic EDE-10P resin† and elution with 0.5 N sulphuric acid at a rate of 0.5 ml cm^{-2} min^{-1}, obtained in the first fraction a 30% hafnium concentrate, with 52% yield of the element, from an orginal 4% concentrate; zirconium dioxide containing less than 0.05% HfO_2 was obtained from the subsequent fractions. With the addition of KCl to the original fluorozirconate solutions, the order of elution of zirconium and hafnium was altered: 40–50% hafnium concentrates, with a hafnium yield of 60–90%, were obtained in the last fractions of the eluates from 8% hafnium concentrates.

In addition to the original fluorozirconate complexes, solutions of chloro-containing complexes of zirconium and hafnium in concentrated hydrochloric acid were also tested[120]. On desorption by the slow passage of 9 M hydrochloric acid, hafnium was eluted first in a fraction with extremely small volume, and effective separation of zirconium and hafnium was achieved.

Vinarov and Shul'gina[121] studied the conditions of separation of zirconium and hafnium on anion-exchange resins produced in the Soviet Union—the weakly basic AN-2F‡ and EDE-10P resins and the strongly basic AV-16§ and AV-17¶ resins. The best separation was achieved using AV-16 resin. Concentration of hafnium in the aqueous phase was observed during sorption on this resin from hydrochloric acid solutions. With sorption on these resins from hydrofluoric acid solutions and subsequent elution with dilute hydrochloric or sulphuric acid, the hafnium is concentrated in the eluates. Thus by sorption on AV-16 and elution with 1 N H_2SO_4, hafnium concentrates with a mean concentration of 50% and a direct yield of hafnium equal to 69% were obtained from the original 29% concentrates.

Thus it has not yet been possible to achieve on anion-exchange resins the high degree of separation of zirconium and hafnium achieved on cation-exchange resins. The good results recently obtained[122] by a combination of chromatography on silica gel and anion exchange on IRA-400 or Dowex-2 are therefore of interest. A two-stage chromatographic process gives purified zirconium dioxide containing less than 0.01% HfO_2, and an enriched hafnium concentrate (Hf : Zr = 40%), which is refined in an anion-exchange resin column to a zirconium concentration of 0.1%.

8. Selective Extraction by Solvents

The methods for separating zirconium and hafnium by selective extraction by solvents (liquid extraction) are the most common in modern technology. Many versions of these methods have been proposed. Examination of the mechanisms of the various extraction processes on the basis of Fomin's classification[123] shows that the methods which are most widely used in industry are those based on extraction by neutral organic reagents, with the formation of the corresponding solvates—selective extraction of hafnium thiocyanates by solvents, chiefly isobutyl methyl ketone (IBMK) and of zirconium nitrates by TBP. We shall examine these versions in most detail. Extraction processes taking place by cation-exchange or anion-exchange mechanisms are also being studied.

(a) Thiocyanate extraction. This method of separation is based on the difference in the distribution constants of the thiocyanato-complexes of zirconium and hafnium between aqueous and organic phases. The technological processes have been developed chiefly by empirical selection of conditions close to the optimal conditions, since there is very little information on the composition and properties of the thiocyanato-complexes of zirconium and hafnium in solution. The composition of the thiocyanato-complexes of zirconium and hafnium was established only recently. According to Golub and Sergun'kin[124], the composition of the thiocyanato-complexes of zirconium and hafnium in aqueous solutions is given by the formula $M(SCN)_n^{4-n}$, where $n = 1-8$. Vinarov and coworkers[125,126] established that the thiocyanato-compounds of zirconium

† EDE-10 is a polyfunctional strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines with epichlorohydrin, and contains $-N(CH_3)_3$ groups (Ed. of Translation).

‡ AN-2F is a polyfunctional, weakly basic anion-exchange resin containing tertiary and secondary nitrogen groups. It is obtained by polycondensation of methyl derivatives of phenol with polyethylenepolyamines and formaldehyde (Ed. of Translation).

§ AV-16 is a polyfunctional, strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines, pyridine, and epichlorohydrin. It contains secondary, tertiary, and quaternary (pyridinium) nitrogen groups (Ed. of Translation).

¶ AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen-groups. It is based on styrene and trimethylamine (Ed. of Translation).

and hafnium which are most readily extracted by acetophenone (APH) from perchloric acid solutions contain the complex anion $[M(SCN)_6]^{2-}$, or under certain conditions have the formula $M(SCN)_4$. The extraction takes place by a solvate mechanism. Sinegribova and Yagodin[127] reported the compositions of the zirconium and hafnium compounds extracted by diisopentyl methylphosphonate (DPMP) from sulphuric acid solutions: $M(OH)_2(SCN)_2.2DPMP$, or $M(OH)_2(SCN)_2.2(DPMP.HSCN)$.

In the original version of the thiocyanate extraction proposed by Fischer and Chalybaeus[128], ammonium thiocyanate and sulphate were added to an aqueous solution of the mixture of zirconium and hafnium sulphates, and the mixture was shaken with diethyl ether in a separating funnel; the hafnium concentrated in the ether phase. Later, a repeated stepwise fractionation was developed[129]. The ether extract obtained as described above was washed with a solution of a mixture of ammonium sulphate and thiocyanate to achieve further selective removal of zirconium into the aqueous phase, after which the zirconium and hafnium were re-extracted with ammonium sulphate solution acidified with sulphuric acid. Zirconium sulphate enriched in hafnium was obtained from the re-extract and passed to the next stage of the fractional extraction. 70–90% concentrates were obtained after 6–8 fractionation stages from a raw material containing 0.5% HfO_2, and 99.6% hafnium specimens were obtained from 60–95% concentrates in an eight-stage extraction scheme.

The process described above for the thiocyanate extraction of hafnium from sulphate solutions is in general fairly efficient, but it also has a number of disadvantages: it is impossible to extract hafnium completely from the raffinates; formation of precipitates is often observed, leading to a decrease in the distribution constants; equilibrium is not established during the experiment in the sulphate scheme, so that the course of the process is influenced to a significant extent by the time for which the original solutions have been left to stand. The first attempts to carry out the thiocyanate extraction from hydrochloric acid solutions[128], however, led to a decrease in the efficiency of separation of zirconium and hafnium, since diethyl ether extracts zirconium preferentially from solutions of the chlorides, so that the presence of chloride ion decreases the degree of enrichment of hafnium in the extract. The use of ether as organic solvent also restricted the possible utilisation of the method on a larger scale, in view of the appreciable solubility of ether in water, its volatility, combustibility, and ability to form explosive mixtures with air.

Because of these features, Fischer and coworkers[130] patented another version of the thiocyanate extraction, in which the distribution of the thiocyanato-compounds of zirconium and hafnium was carried out in the absence of sulphate ions at a low concentration of chloride ions in the original solutions, as a result of which reproducible equilibrium was established in the system and precipitates were not formed. Although the authors, as before, used chiefly diethyl ether, they also noted the possibility of using certain other solvents for this process: n-butanol, cyclohexanone, n-butyl acetate, pentyl acetate, methyl propyl ketone, ethyl isopropyl ketone, and benzaldehyde. The distribution and separation of thiocyanato-compounds of zirconium and hafnium during extraction by hexanone was studied in detail[131].

The separation of zirconium and hafnium in a multistage countercurrent continuously operating apparatus has also been described[132]. The liquid phases are solutions of thiocyanic acid in water and in hexane. The solid salts—mixtures of zirconium and hafnium tetrachlorides or oxide chlorides—are introduced continuously into the middle stage of the distribution cascade. The aqueous phase or raffinate obtained contained purified zirconium with an Hf concentration down to 3×10^{-4}%,

Hoshino Yoshio[133] studied the distribution constants for zirconium and hafnium between an aqueous phase containing NH_4SCN, $(NH_4)_2SO_4$, and HCl, and 80 oxygen-containing solvents: ketones, alcohols, esters, and ethers. The highest distribution constants were obtained using alicyclic ketones. In some papers by Hoshino Yoshio and Ito Takuii[134,135], preference is given to extraction by cyclohexanone, which gives high values for the separation factor (β) for zirconium and hafnium (up to 250). The same solvent was previously used by Motov and Leshtaeva[136,137] to obtain zirconium dioxide purified from hafnium, together with hafnium concentrates (the values of β reached 140).

Yagodin, Kaplan, and coworkers[138-140] successfully separated thiocyanato-compounds of zirconium and hafnium by selective extraction by diisopentyl methylphosphonate (DPMP), diluted with benzene or xylene, from sulphuric or nitric acid solutions of zirconium and hafnium. Diviš[142] studied the selective extraction of the thiocyanato-compounds by methylcyclohexanone. No data on the industrial application of the above versions of the thiocyanate extraction have been published, however. We shall therefore not deal with these in more detail, but shall consider the method of separating zirconium and hafnium by selective thiocyanate extraction using isobutyl methyl ketone (IBMK, hexone), which is widely used at the present time[8,11,143-149]. Using this method, conditions have been found for effective extraction from hydrochloric acid solutions; this proved difficult in the first years after the development of the thiocyanate extraction by Fischer.

In one of the latest industrial versions of this method[8,11], a mixture of zirconium and hafnium tetrachlorides or oxide chlorides, obtained from "ore" raw material containing 2% HfO_2 in $(Zr, Hf)O_2$, is dissolved in water to which ammonium thiocyanate has been added. The concentrations of the components in the original solution are as follows: 1.3 M metal, 2.8 M NH_4SCN, and 1 N free acid; the IBMK extracting agent contains 2.8 M HSCN. The extraction, washing, and re-extraction are carried out in continuously operating countercurrent columns. The extract containing enriched hafnium concentrate and thiocyanic acid is washed with 3.5 M HCl; this is accompanied by additional removal of part of the zirconium. The hydrochloric acid wash solution is combined with a new portion of the original solution. The washed extract passes to a system of re-extraction columns, where the hafnium product is washed out with 5 N sulphuric acid. Ammonia is added to precipitate hafnium hydroxide containing small quantities of zirconium, titanium, boron, cadmium, etc.; if a pure product is required, further purification is carried out by re-pulping the product in hydrochloric acid, precipitating hafnium phthalate, re-pulping with aqueous ammonia, drying, and heating the hafnium hydroxide residue. The extracting agent and NH_4SCN (after regeneration from the ammoniacal solution) are used again.

The thiocyanic acid present in the raffinate is also extracted in a countercurrent system with pure IBMK, from which it is then re-extracted with water; the solution obtained is used for the preparation of the original solution for extraction, or the IBMK and HSCN are used

in a new extraction. Zirconium is regenerated by diluting the raffinate to a (Zr, Hf)O_2 concentration of ~ 12 g litre^{-1}, precipitating zirconium sulphate at pH 1.4–1.8 and 60–70°C, re-pulping the basic sulphate precipitate with aqueous ammonia, and heating the zirconium hydroxide. Purified zirconium dioxide and hafnium dioxide are obtained on the industrial scale by this method.

(b) Extraction by TBP and other alkyl phosphates. The method of extraction by TBP, first developed and used in France, is now being developed and extended on an increasing scale [6,11]. The method is based on the difference in the distribution constants of zirconium and hafnium nitrates in extraction by dilute TBP. Zirconium is extracted much more readily than hafnium, so that zirconium is concentrated in the extract, and hafnium in the raffinate. The theoretical principles of the separation of zirconium and hafnium by extraction using TBP are dealt with in a large number of papers by Huré, Korovin, Rozen, and others [75,76,150-154]. The extraction takes place by a solvate mechanism. The composition of the solvates formed during extraction may be different under different conditions. For the conditions usually employed in the separation of zirconium and hafnium, the mechanism of extraction can be represented as follows [75,76]:

$$(Zr, Hf)O^{2+} + 2H^+ + 4NO_3^- + 2\,TBP \rightleftarrows (Zr, Hf)(NO_3)_4 \cdot 2\,TBP + H_2O$$

or, with allowance for the hydration of zirconium and hafnium in the aqueous phase [150]:

$$[(Zr,Hf)(OH)_2]^{2+} + 2H^+ + 4\,NO_3^- + 2\,TBP \rightleftarrows (Zr,Hf)(NO_3)_4 \cdot 2\,TBP + 2H_2O\ .$$

From this it follows that the Zr : Hf ratio in the equilibrium organic phase in extraction from their mixtures is greater than that in the aqueous phase.

In the original version of the method, developed by Huré and Saint-James [155], the extraction was carried out with a mixture of TBP and white spirit (volume ratio 60 : 40), acidified to 1.6 M HNO_3; the original solution contained 30 g litre^{-1} Zr(Hf), 3 M HNO_3, and 3.5 M $NaNO_3$. The separation factor for the extraction was ~ 10. The washing was carried out with a mixture of 3 M HNO_3 and 3.5 M $NaNO_3$. The process was carried out in a system of mixing and settling vessels. Four extraction theoretical plates and two washing theoretical plates were required in order to obtain zirconium containing less than 0.02% hafnium, in 90% yield from the original ore raw material. The final aqueous phase contained 20–40% hafnium, relative to the total hafnium and zirconium.

The principles of the technology of the separation of zirconium and hafnium by extraction using TBP, developed at Harwell (England), are given in reviews by Hudswell and Hutcheon [75,76]. The extraction was carried out from an original solution of the nitrates, containing 80 g litre^{-1} zirconium and 1.6 g litre^{-1} hafnium in 8 M HNO_3. A 50% solution of TBP in xylene was used as extracting agent. A system of 4 extraction plates and 6 washing plates gave a high yield of zirconium with low hafnium concentration, together with ~ 25% hafnium concentrate. When kerosene (or decalin [156]) was used as diluent for the TBP, a third phase appeared, complicating the process.

Various extractors have been described [156-159] for the separation of zirconium and hafnium by extraction using TBP (vibrational columns, mixing and settling vessels, etc.). Much information has been published [147,159-173] on various versions of the extraction using these solvents. There are also a few data on extraction by TBP from sulphuric acid solutions [170]; the presence of thiocyanate ion is necessary. Hafnium is concentrated in the organic phase, but the separation factors are low.

Let us consider in slightly more detail one modern version of the extraction by TBP (the "nitrophos process"), developed in the USA. Initially, Cox and coworkers [159] used for the extraction a mixture of TBP and heptane (60 : 40), acidified to 0.65 *N* HNO_3; the original solution of zirconium and hafnium nitrates did not contain salting-out agents, and its acidity corresponded to ~ 5 M HNO_3. The separation factor was ~ 15. 14 working stages of the mixing and settling vessels (equivalent to 12 theoretical plates) gave zirconium containing less than 0.01% hafnium, together with a ~ 44% hafnium concentrate. The separation of zirconium and hafnium was carried out on the pilot-plant scale under slightly modified technological conditions [160].

An original solution of 1 M zirconium nitrate, with acidity 8 M HNO_3, and Hf : (Hf + Zr) ratio = 2%, was prepared. The solution was passed to the middle section of the column and moved downwards, in the opposite direction to a mixture of TBP and n-hexane (1 : 1), saturated beforehand with nitric acid by mixing with 8 M HNO_3. The extract then passed into the upper half of the column, where it was washed in a countercurrent process with 5 M HNO_3. The re-extraction was carried out in a special countercurrent column using de-ionised water. The re-extract contained purified zirconium with ≤ 0.006% hafnium, and the raffinate contained a 90–95% hafnium concentrate. The ratio of the volumes of solutions entering the system, the original organic solvent, the wash solution, and the re-extracting water was 1 : 3.6 : 0.6 : 0.9.

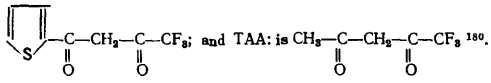
On the industrial scale, the "nitrophos process" is carried out in stainless steel columns. The concentration of zirconium nitrate in the original solution is 0.6 M, and the ratio of the volumes of the above solutions is 1 : 2.8 : 1.8 : 1.2. A mixture of saturated and unsaturated hydrocarbons is used to dilute the TBP.

Approximate calculations of the main data for extraction apparatus for the separation of zirconium and hafnium by extraction with TBP are given by Benedict and Pigford [174]. Granovskii, Komissarova, Nalimov, and others [175-177] have begun the development of a mathematical model for this process in order to determine its optimal conditions. The use of modern mathematical methods of optimisation in such complicated processes as the separation of zirconium and hafnium is undoubtedly extremely promising.

In addition to the improvement of the method of extraction by TBP, the search for other equally effective extracting agents is of interest. In particular, it has been suggested that zirconium and hafnium may be separated by extraction from nitrate solutions using other alkyl and aryl phosphates [166]. Separation by oxygen-containing solvents such as 3-methylbutanol, n-hexanol, methyl propylketone, etc. has been tried [178]; from 4 *N* HNO_3, these solvents extract 50–60% zirconium and hafnium, with separation factors of 6–9. In extraction by acetophenone from hydrochloric acid solutions with an acidity of 10 M, the maximal separation factors for zirconium and hafnium reach the value 5. All of these methods have as yet been little developed and are of no industrial importance.

(c) Extraction by fluorinated β-diketones. Thenoyltrifluoroacetone or thiophencarbonyltrifluoroacetone (TTA), trifluoroacetylacetone (TAA), and various

other fluorinated β-diketones react with zirconium and hafnium to form inner-complex compounds (chelates), soluble in benzene and various other solvents. The general formula for the fluorinated β-diketones can be written: $R-COCH_2-CO-CF_3$, where R represents various radicals; for example, TTA is:



and TAA: is $CH_3-C(=O)-CH_2-C(=O)-CF_3$ [180].

Complex formation by zirconium and hafnium with β-diketones has been studied by many authors [181-183]. The extraction of zirconium and hafnium can be represented in general form as follows:

$$Zr\,(Hf)^{4+}_{aq} + 4HK_{org} \rightleftarrows (Zr,Hf)\,K_{4\,org} + 4H^{+}_{aq}$$

where HK represents the fluorinated β-diketone and the subscripts aq and org denote the aqueous and organic phases. These reactions are often complicated by hydrolysis and polymerisation of the zirconium and hafnium ions. The differences in the distribution constants of zirconium and hafnium complexes make it possible to separate these elements by selective extraction [183-187]; zirconium is concentrated in the organic phase. According to Huffman [187], the separation factors obtained using a solution of TTA in benzene amount to 25; figures of 13-18 are obtained for various other extracting agents of the same class. Despite the fairly high separation factors, extraction by β-diketones cannot find extensive industrial application until these extracting agents become much more readily available.

(d) Extraction by liquid sorbents. Laboratory experiments on the separation of zirconium and hafnium by extraction using liquid sorbents of the cation-exchange (alkyl hydrogen phosphates) and anion-exchange (amines) types have been described in recent years. The mechanism of these separation processes is in principle similar to those on solid ion-exchange resins.

In extraction by solutions of alkyl hydrogen phosphates in organic solvents, salts of the cations being extracted (zirconium or hafnium) with the anions of the organic acids are formed.

Extraction by the acid esters of orthophosphoric acid—dihexyl, diheptyl, dioctyl, and diphenyl hydrogen phosphates—from sulphuric acid solutions showed that hafnium is concentrated in the organic phase [140,188]. In extraction by 50% solutions of these acids in xylene from a solution containing 20 g litre^{-1} Zr(Hf) in 2 N H_2SO_4, the separation factor reaches the value 12. Better results—separation factors up to 20—were achieved by extraction using di-2-ethylhexyl hydrogen phosphate. Zirconium is extracted preferentially from hydrochloric acid solutions [189].

In the extraction of zirconium and hafnium by solutions of amines, salts of the anions being extracted with organic cations are formed. For example, the mechanism of the extraction of zirconium and hafnium from solutions of their fluoro-complexes by trioctylamine (TOA) can probably be represented [190]:

$$2\,(NR_3H)\,HSO_{4\,org} + K_2MF_{6\,aq} \rightleftarrows (R_3NH)_2MF_{6\,org} + 2\,KHSO_{4\,aq}$$

where $R = C_8H_{17}$.

The study of extraction from hydrochloric acid solutions using primary, secondary, and tertiary amines [191,192] has shown that zirconium is concentrated in the organic phase. The separation factors vary over a wide range, from 1 to 89, depending on the conditions. Tertiary amines are the most selective. In extraction by a 0.1 M solution of TOA in cyclohexane from 7-9 M HCl solutions of zirconium and hafnium, the separation factor had values of 22-29. Decrease in temperature to ~ 10°C increased the separation factor to 70-89, but the degree of extraction was reduced. A sharp increase in the separation factor to 65-77 was achieved by adding HNO_3 to the original solution. In extraction by trioctylamine in xylene from sulphuric acid solutions with an acidity greater than 1 N, [140] zirconium was also extracted preferentially, with a separation factor of 10. In extraction from acidic solutions of fluorozirconate and fluorohafnate, the separation factor did not exceed 5.

Thus the use of liquid sorbents for the separation of zirconium and hafnium has proved effective, and continuation of these studies appears desirable.

III. FUTURE PROSPECTS FOR THE APPLICATION OF THE MOST IMPORTANT METHODS FOR SEPARATING ZIRCONIUM AND HAFNIUM

The above data make possible a comparative estimate of the future prospects for the industrial application of various methods for separating zirconium and hafnium. Since the present review did not give detailed technical-economic calculations on individual technological methods (for a number of methods these calculations have not been carried out), such a comparative estimate can obviously be made here only in the most general form. The basic criteria for the selection of methods or a combination of methods should be as follows: the highest separation factors, highest specific capacity of the apparatus, simplicity in the technological process and in the apparatus required, the possibility of carrying out a continuous process, low cost of the raw material and reagents used, and the possibility of obtaining them in the required quantities. Another important problem concerns the most rational way of introducing the separation of zirconium and hafnium into the general scheme for the production of these metals from the ore raw material.

If we examine on this basis the future prospects for the application of the above processes for the separation of zirconium and hafnium in industry (most of them can be used for small-scale preparative laboratory separation), it immediately becomes necessary to reject almost all methods of fractional crystallisation or precipitation, because of the low separation factors and the tedious and time-consuming nature of the technological processes, and also the inefficient (in present form) methods of selective dechlorination and electrolysis. Here an exception is the method developed by Sazhin and Pepelyaeva for the fractional crystallisation of potassium fluorozirconates and fluorohafnates, where the simplicity of the technology of separation and its successful combination with the method for opening zircon will evidently enable it, within a short time, to compete successfully even with other more effective separation processes, for the production of zirconium dioxide purified from hafnium. The method of selective reduction of the chlorides by metals is of considerable interest, since it uses zirconium and hafnium chlorides, obtained in the opening of zircon by the efficient chlorination method, and eliminates completely the intermediate hydrometallurgical stages in the production of zirconium and hafnium. This method, however, apparently still requires further technological development. The same

is true of the effective method of separation by fractional distillation under pressure, but the rapid development of this method can take place only after the optimal solution has been found to the problems of selecting constructional materials and a rational design of apparatus for the process. The method of separation on silica gel, although in general fairly effective, has an important disadvantage which makes its extensive industrial application difficult, namely the use of methanol, which is very toxic.

Of the ion-exchange methods, cation exchange on the sulphonic acid cation-exchange resins Dowex-50, KU-2, etc. has found most extensive application, thanks to the high separation factors, the availability of the resins and reagents used, and the possibility of setting up a continuous countercurrent process. The specific capacity of the ion-exchange apparatus (calculated on unit cross-sectional area or volume) and the concentration of zirconium and hafnium in the solutions obtained are usually low, however. Thus on the industrial scale of production it is necessary to have batteries of large-scale columns and to pass comparatively large volumes of solutions through these columns, and this naturally restricts the possible application of the ion-exchange method. This method, however, may even become the predominant method for the industrial separation of zirconium and hafnium, when conditions are found for the highly selective sorption of hafnium by ion-exchange resins. At present, however, the most promising field of application of the ion-exchange method for the separation of zirconium and hafnium is evidently to be found in the treatment of high-percentage hafnium concentrates and the refining of hafnium and zirconium specimens.

The methods of selective extraction by solvents, particularly IBMK and TBP, are widely used in industry. The advantages of these methods are the high separation factors, the high concentrations of the zirconium and hafnium solutions, the high specific capacity of the apparatus, the possibility of using continuously operating countercurrent extractors, etc. By selecting a suitable version, extraction methods can be used for the treatment of hafnium concentrates obtained by any of the existing methods for opening ore concentrates (zircon, etc.). The chief disadvantage of extraction methods is the relatively high cost of the reagents. Thus one of the most important tasks facing industries producing pure specimens of zirconium and hafnium must be the further improvement of the technology of extraction separation processes, including the search for the most readily available and at the same time highly efficient complex-forming reagents and extracting agents.

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THE RADIOCHEMICAL PREPARATION OF ION-EXCHANGE MATERIALS

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The preparation of ion-exchange materials under the influence of ionising radiation is one of the few radiochemical processes which has found definite practical application. Thus homogeneous ion-exchange membranes have been obtained by grafting certain monomers on to various polymer-carriers under the influence of radiation[1-9]. These membranes have distinct advantages over those prepared by ordinary chemical methods. Moreover, ion-exchange resins prepared by the radiochemical method are in a number of instances not only better, but also cheaper, than ordinary standard ion exchangers[10].

The methods of radiation polymerisation, copolymerisation, and grafting have recently become fairly widespread, since they make it possible to prepare materials which differ from ordinary materials in their high purity, improved physicomechanical characteristics, and other valuable properties influencing their performance.

Grafting under the influence of radiation makes it possible in certain instances to obtain graft copolymers whose preparation is difficult or impossible by ordinary chemical methods. These copolymers can be used to prepare ion-exchange membranes with high mechanical strength, high selectivity, and low electrical resistance. All these features are responsible for the considerable interest in the radiochemical preparation of ion-exchange resins, the progress made in this field, and methods for its further development.

1. MEMBRANES

Most ion-exchange membranes are based on graft copolymers, so that it is convenient to examine briefly radiochemical methods for their preparation, and also the advantages and disadvantages of graft copolymers prepared under the influence of radiation, relative to ordinary copolymers.

The main radiochemical methods for the preparation of graft copolymers are as follows[11-26]: (*a*) direct grafting by irradiation of the polymer–monomer system; (*b*) grafting on to a polymer which is irradiated in a vacuum and then brought into contact with the monomer; (*c*) grafting on to a polymer irradiated in air with heating in a medium of the monomer; (*d*) intermolecular cross-linking of two polymers in the solid state, molten state, or solution; (*e*) grafting by the irradiation of emulsions or suspensions consisting of two polymers, or a polymer and a monomer; and (*f*) grafting under the influence of localised neutron irradiation.

It should be noted that in the preparation of graft copolymers by any of the above methods, block copolymers are also formed. As a rule, however, the relative quantity of block copolymers is extremely small; moreover, it is often impossible to decide whether a given copolymer should be described as a block copolymer or a graft copolymer[12,17]. The separation of block and graft copolymers also involves considerable methodological difficulties[27].

The efficiency of radiochemical grafting is determined by many factors, such as the nature of the polymers and monomers, the integral dose, the dose rate, temperature, the dimensions of the specimens being irradiated, the degree of crystallinity and phase state of the polymers, the rate of diffusion of the monomers in the polymers, the compatibility of the polymers making up the graft copolymers, the ability of the polymers to undergo swelling in the monomers, etc. The dependence of the rate of formation of graft copolymers on the above factors is so complex and varied that we can indicate only a few of the most general regular features, which may prove useful in an examination of problems related to the radiochemical preparation of ion-exchange membranes.

The preparation of graft copolymers by method (*a*) is at present the most widespread. The efficiency of the grafting is here determined chiefly by the quantity G_p/G_m where G_p/G_m are the yields of radicals on irradiation of the polymer and monomer respectively. The greater this quantity, the smaller the quantity of homopolymer formed. In this respect, the best system is the polyethylene–styrene system, for which $G_p/G_m \simeq 2-10$. The chief disadvantage of method (*a*) is that a large quantity of homopolymer is usually formed. The greater part of the ion-exchange membranes prepared by the radiochemical method are obtained, however, by this method.

One version of method (*a*) is vapour-phase radiochemical grafting, in which a large quantity of homopolymer is not formed[28-37]. Moreover, this method makes possible efficient grafting even when the quantity G_p/G_m is less than unity. The method of vapour-phase radiochemical graft polymerisation eliminates completely the possibility of capillary condensation in the pores and thus makes it possible to carry out grafting not only on organic polymers, but also on inorganic carrier-supports[28-34].

In grafting by method (*b*), almost no homopolymer is formed, but the rate of grafting is low, since the greater part of the macroradicals are destroyed on heating before they are able to initiate graft polymerisation. This method is seldom used to obtain ion-exchange membranes.

Method (*c*) is usually employed for surface grafting. By using sufficiently thin films and low irradiation dose rates, however, it is possible to introduce oxygen-containing groups throughout almost the entire volume of the polymer, and hence to achieve more or less uniform grafting. The disadvantages of the method include a slight deterioration in the physicomechanical properties of the carrier-polymer as a result of its radiochemical oxidation, and also the formation of an appreciable quantity of homopolymer under the influence of the $\cdot OH$ radicals produced by the thermal decomposition of polymeric hydroperoxides. It is possible, however, to avoid formation of the homopolymer by carrying out the decomposition of the hydroperoxides and the grafting in the presence of iron(II) salts[38]. This prevents the formation of the $\cdot OH$ radicals which inititate the homopolymerisation:

$$ROOH + Fe^{2+} \rightarrow RO\cdot + Fe^{3+} + OH^-.$$

Method (*c*) is fairly frequently used to obtain ion-exchange membranes.

Method (*d*) is usually characterised by low yields of block and graft copolymers, and involves considerable methodological difficulties. Attempts have been made to use this method to prepare ion-exchange membranes[26,39,40], but because of the high integral doses (500 Mrad) and highly brittle nature of the product, these materials are significantly inferior to membranes prepared by methods (*a*) or (*c*).

Methods (*e*) and (*f*) are usually characterised by a high selectivity of graft (or block) copolymer formation, accompanied in most instances by only slight homopolymer formation. Nevertheless, these methods have not found practical application, not only in the preparation of ion-exchange membranes but also in the chemistry of graft copolymers in general, because of the marked experimental difficulties.

The problem of chemical bond formation during grafting is of considerable importance for the quality of membranes prepared by the radiochemical method. The chief method for detecting the presence of graft copolymers involves extraction of the homopolymers with suitable solvents. When the molecular chains of two different polymers are closely intertwined, however, removal of one of them by means of solvents may be impossible[41]. This forms the basis of the preparation of inter-polymer membranes, which have found extensive application in laboratory studies[42-44].

A more reliable method for the identification of graft copolymers is by fractional precipitation of the individual components from solutions containing a mixture of the homopolymers and graft copolymers[45,46]. This method has been used to prove the formation of a poly(ethylene-graft-styrene) system, which subsequently formed a basis for the preparation of membranes containing $-SO_3H$ and $-CH_2N^+(CH_3)_3$ groups, with improved properties influencing performance[47]. Methods which can be used in addition to fractional precipitation and selective extraction include the following[48,49]: fractional dissolution, selective precipitation, turbidimetric titration, adsorption chromatography and elution, ultracentrifuging, etc. In most work on the radiochemical preparation of ion-exchange membranes, however, these methods are not used, and the presence of graft copolymers is usually established merely on the basis of data obtained by selective extraction.

The radiothermoluminescence method[50-52] can apparently be used in certain instances to detect the presence of chemical bonds in graft copolymers.

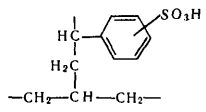
The quality of membranes based on graft copolymers should be higher than that of membranes prepared from a mixture of homopolymers. These membranes have a greater homogeneity and uniformity of composition, higher chemical resistance and mechanical strength, and superior ion-exchange and electrochemical characteristics. For a given quantity of graft polymer, the properties of the system, particularly its homogeneity, will generally be better, the shorter the graft chains. Non-uniformity is one of the main disadvantages of ion-exchange membranes based on graft copolymers.

The distribution of a graft polymer within the volume of a carrier-polymer can be estimated by a microinterferometric method[53]. The superior properties of membranes prepared by the radiochemical method, and their greater uniformity compared with ordinary membranes may be due to the greater probability of formation of true graft copolymers during irradiation, compared with chemical initiation.

As already noted, the chief disadvantage of both ordinary membranes and membranes prepared under the influence of radiation is non-uniformity of composition. This may be due to the presence of amorphous and crystalline regions or regions with different degrees of orientation, and also to the varied supermolecular structures of the polymers on to which the grafting is carried out. Such important factors, determining the efficiency of graft polymerisation, as the yield of radicals, the degree of swelling, the rate of diffusion of the monomers, the reaction rate constants for termination of the growing polymer chains, and various others, differ significantly in the crystalline and amorphous regions. In most instances, the rate of grafting on amorphous polymer specimens is high, and the copolymers obtained are fairly homogeneous, but the generally unsatisfactory physicomechanical properties of these products prevents their extensive application. The degree of crystallinity may change during grafting; for example, it sometimes decreases with increase in the quantity of graft polymer[54]. For each specific system, there apparently exists a definite degree of crystallinity at which membranes with optimal physicomechanical and electrochemical properties are obtained. Studies in this direction are still in the initial stages.

When ion-exchange groups are introduced into a graft copolymer, its non-uniformity may increase. The formation of hydrophilic and hydrophobic regions in the membranes is accompanied by partial separation into layers, a decrease in selectivity, and an increase in the water-permeability of the membranes. The probability of this undesirable process is much smaller, however, for membranes prepared by radiochemical methods, and this ensures satisfactory properties influencing performance.

Most studies of the radiochemical preparation of cation-exchange membranes have been carried out using the poly(ethylene-graft-styrene) system. Direct irradiation, with ^{60}Co γ-radiation, of polyethylene films immersed in liquid styrene, followed by sulphonation of the poly(ethylene-graft-styrene) system with sulphuric or chlorosulphonic acids and subsequent hydrolysis with alkali has been used to prepare strongly acidic homogeneous membranes[9,40,47,55-64], apparently having the following structure:



The efficiency of grafting is increased considerably by preliminary vacuum-treatment of the polyethylene–styrene system[40,57] or by irradiation of the system in an atmosphere of nitrogen[47,58].

It has been shown[7,9,40,56] that the optimal quantity of polystyrene in the graft copolymer should not exceed 20–40 wt. %. Membranes containing more than 50 wt. % polystyrene, despite their low specific volume electrical resistance, are too brittle, and unsuitable for prolonged use.

To obtain copolymers with a high polystyrene content, a small quantity of divinylbenzene is sometimes added to the styrene; this decreases considerably the degree of swelling of the resulting membranes and improves their physicochemical properties[56,57].

To obtain homogeneous membranes, the styrene is grafted on to polyethylene powder, film, or granules, and the graft copolymers are then subjected to hot rolling. It is claimed[62] that this method has certain advantages over those described above, since it gives fairly homogeneous membranes, and this is extremely important not only in the radiochemical but also in the ordinary methods of preparation.

In all the work cited above[9,40,47,55-64], the irradiation was carried out at dose rates in the range 4–100 rad s^{-1}. The integral doses required to obtain graft copolymers with optimal composition varied from tenths of an Mrad to several Mrad.

The membranes obtained had the following characteristics: capacity 1.5–2.5 mg-equiv. g^{-1}; resistivity 50–200 Ω cm; selectivity 97–98%; and tensile strength 100–200 kgf cm^{-2}. The membranes were characterised by improved properties influencing performance. For example, the energy consumption for the desalination of water by electrodialysis was less for membranes prepared by the radiochemical method than for membranes prepared by ordinary methods (Fig. 1).

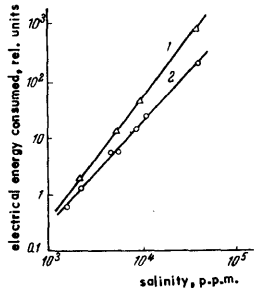


Fig. 1. Desalination of water. Dependence of the consumption of electrical energy on the salinity of the water[47]: 1) for ordinary membranes; 2) for membranes prepared by the radiochemical method.

The efficiency of grafting was greater for high-density polyethylene[45,55] and when thicker films were used[40,45,55,65]. This may be due to a decrease in the reaction rate constant for bimolecular termination of the growing polymer chains or to a change from bimolecular termination to linear termination under these conditions.

The presence of stabiliser (diphenylamine) in the polyethylene film decreases the yield of graft copolymer and the efficiency of grafting[40]. It is therefore better to use non-stabilised polyethylene film.

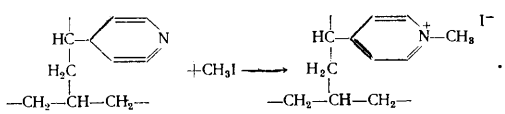
The addition of other monomers, for example acrylonitrile (10–20 wt. %), sometimes increases the elasticity of the membranes considerably. Thus a sulphonic acid membrane based on the poly[ethylene-graft-(styrene-co-acrylonitrile)] system is elastic even in the dry state, whereas the analogous membrane based on poly(ethylene-graft-styrene) can be kept only in the swollen state[59].

Certain solvents, in particular methanol, increase considerably the efficiency of graft polymerisation and make it possible to decrease significantly the doses required to achieve the optimal degree of grafting[59,66].

Some data[40,55] indicate an increase in the efficiency of the grafting of styrene on to polyethylene with decrease in temperature, but other results[14,41] indicate the opposite. In the preparation of ion-exchange membranes, there is evidently in each specific instance an optimal temperature, determined by many of the parameters characterising the system being irradiated.

A number of anion-exchange membranes containing quaternary ammonium groups[47,55,56,61,62] or secondary and teriary amino-groups[61] have been prepared from poly(ethylene-graft-styrene) systems obtained by direction irradiation. The first stage usually involves chloromethylation with mono-chloromethyl ether at the boiling point in the presence of tin(IV) chloride as catalyst and this is followed by amination by heating with a 25% solution of trimethylamine in methanol[47]. These membranes have the following characteristics: capacity 1.5–2 mg-equiv. g^{-1}, resistivity 100–200 Ω cm, selectivity 95–97%, and tensile strength 150–300 kgf cm^{-2}.

Weakly basic and weakly acidic membranes can be prepared by grafting monomers such as 4-vinylpyridine[7,56,64] or acrylic acid[57] on to polyethylene. Treatment of the poly(ethylene-graft-4-vinylpyridine) system with alkylating agents leads to the formation of strongly basic membranes[7,56,64]:



Macromolecular compounds other than polyethylene can also be used as carrier-polymers for the preparation of membranes. Methods have been described for the preparation of membranes based on poly(vinyl chloride-graft-styrene)[57], poly(tetrafluoroethylene-graft-styrene)[57,61], poly[(ethylene-co-propylene)-graft-styrene][59], poly(tetrafluoroethylene-graft-acrylic acid)[67,68], and poly(tetrafluoroethylene-graft-4-vinylpyridine)[67,68] systems obtained by direct irradiation. When the polymer does not undergo swelling in the monomer (polytetrafluoroethylene–styrene), satisfactory results are obtained by periodic irradiation[57]. In this way it is possible to achieve a high degree of grafting throughout the entire volume of the polymer. The direct action of ^{60}Co γ-radiation on polytetrafluoroethylene film in aqueous acrylic acid solutions containing $FeSO_4$ as homopolymerisation inhibitor made it possible to graft 10–20 wt. % polyacrylic acid[67,68]. These films had a high homogeneity, underwent uniform swelling in water, and were suitable for use as cation-exchange membranes.

Weakly acidic and strongly basic membranes[69-71], with excellent properties influencing performance, were prepared by grafting methyl methacrylate, ethyl acrylate, and acrylonitrile from the vapour phase on to polyethylene films, followed by alkaline hydrolysis of the ester and nitrile groups to carboxylate groups, or by grafting 4-vinylpyridine and 2-methyl-5-vinylpyridine, followed by alkylation of the products. The grafting was carried out at room temperature in the absence of atmospheric oxygen under the influence of ^{60}Co γ-radiation, at a dose rate of 2 rad s^{-1}. The doses required to achieve extensive degrees of grafting did not exceed 1 Mrad. Thus irradiation with a dose of 0.4 Mrad was sufficient to give poly(ethylene-graft-4-vinylpyridine) containing 70% graft poly(4-vinylpyridine). The capacity of this membrane after alkylation amounted to ~ 4 mg-equiv. g^{-1}.[69]

The method of vapour-phase radiochemical grafting was used to prepare copolymers based on polyethylene powder (100 mesh), which was irradiated with ^{60}Co γ-radiation at 0.5 rad s^{-1} or with a beam of accelerated electrons at 6×10^4 rad s^{-1} at 80°C in the presence of the vapours of methyl acrylate, ethyl acrylate, 4-vinylpyridine, 2-methyl-5-vinylpyridine, styrene, and vinyl acetate[72,73].

The efficiency of grafting for equal doses was greater when γ-rays were used than when a beam of accelerated electrons was used. The degree of grafting decreased in the following order: methyl acrylate > styrene > ethyl acrylate > 4-vinylpyridine > 2-methyl-5-vinylpyridine > vinyl acetate. These graft copolymers were then converted at 120°C and a pressure of 200 kgf cm^{-2} into films with thickness 0.1–0.2 mm. Treatment of poly(ethylene-graft-4-vinylpyridine) and poly(ethylene-graft-2-methyl-5-vinylpyridine) films with a $CH_3I + CH_3NO_2 + (CH_3)_2CO + C_2H_5OH + O(C_2H_4)_2O$ mixture gave membranes of the quaternary pyridinium type with a capacity of ~ 2 mg-equiv. g^{-1}. Sulphonic acid membranes were prepared by sulphonating poly(ethylene-graft-styrene) with conc. H_2SO_4 in the presence of Ag_2SO_4 at 30–100°C. Carboxylic acid membranes were prepared by hydrolysing poly(ethylene-graft-methyl acrylate) and poly(ethylene-graft-ethyl acrylate) with a 1 *N* solution of KOH in alcohol. In almost all instances the functional groups of the graft copolymers were converted almost completely into ion-exchange groups. Copolymers with a very low concentration of the graft polymer were an exception.

It has been noted[60,74-77] that membranes with a high uniformity of composition cannot be obtained by direct grafting. Uniformity is achieved by preliminary radiochemical oxidation of the polymer, followed by grafting with heating†.

The method of preliminary irradiation of the polymer in a vacuum or in an atmosphere of an inert gas, followed by treatment of the irradiated product with monomer, has also been used to prepare ion-exchange membranes[60,77-80]. Thus irradiation of polyethylene film by ^{60}Co γ-rays in an atmosphere of nitrogen (integral dose 0.3 Mrad, dose rate

† It has also been noted[40], however, that the peroxide method is unsuitable for the preparation of a graft copolymer with a sufficiently high degree of grafting.

60 rad s^{-1}) followed by heating at 40°C in styrene gives a graft copolymer containing up to 30% polystyrene. Subsequent treatment of this film with chlorosulphonic acid and alkali gives a fairly uniform membrane with a capacity of 1.6 mg-equiv. g^{-1} and resistivity 250–300 Ω cm.[60] By altering the conditions of irradiation and grafting, it is possible to prepare membranes with varied physicochemical and physicomechanical properties.

Irradiation with ultraviolet light has also been used to obtain block copolymers for the preparation of ion-exchange membranes[81-83]. Thus the copolymerisation of dibutyl vinylphosphonate and acrylic acid has been carried out under the influence of ultraviolet light. This copolymer was dissolved in alcohol, a cross-linking agent (triallyl cyanurate) was added, and the solution was used to prepare a film, irradiation of which gave a membrane which was insoluble in water but underwent swelling to the extent of 10–40%, and had a capacity with respect to Fe^{3+} equal to 9–12 mg-equiv. g^{-1}.[82] Membranes with satisfactory properties influencing performance were obtained by ultraviolet irradiation of systems containing butyl vinyl sulphonate, vinyl acetate, and ethyleneglycol dimethacrylate[83] or salts of styrenesulphonic acid and acrylic or methacrylic acids[81].

Irradiation with accelerated electrons (dose 5 Mrad) of glass fibre in a solution containing ethyl acetate, polyethyl acrylate, and divinylbenzene[9,84] was used to prepare a reinforced homogeneous membrane. The ester groups were hydrolysed with concentrated alkali solutions.

Membranes obtained by the copolymerisation of styrene and tetrafluoroethylene have particularly high mechanical strength, chemical resistance, and heat resistance[9,61]. Ion-exchange groups are introduced into these membranes by the usual methods.

In the preparation of ion-exchange membranes, the use of radiation is not restricted to the initiation of block and graft copolymerisation. There are data indicating the promising possibilities of using radiation for the formation of three-dimensional insoluble structures containing ion-exchange groups[85]. Thus the irradiation, with ^{60}Co γ-rays (dose 10 Mrad), of films of a copolymer of styrene and butadiene, followed by treatment with conc. H_2SO_4, gave homogeneous membranes of fairly high quality[9,86]. The irradiation, by ^{60}Co γ-rays (dose 30–150 Mrad) and accelerated electrons (dose 150–500 Mrad), of block copolymers of salts of styrene sulphonic acid and acrylic acid was accompanied by the formation of membranes with a capacity of 3–10 mg-equiv. g^{-1}, which were insoluble but underwent swelling[81]. As already noted, the preparation of membranes by the irradiation of a mixture of polyethylene and polystyrene is not promising, because of the high values of the integral doses and the poor physicochemical characteristics of the membranes[40,87]. The same disadvantages are shown by membranes obtained by sulphonating polystyrene films, cross-linked by irradiation[88].

Irradiation of heterogeneous ion-exchange membranes may improve their properties. Thus the durability of membranes based on KU-2 resin‡ and polyethylene is increased by irradiation[40]. Radiochemical vulcanisation is a fairly promising process for heterogeneous membranes consisting of ion-exchange resins and rubbers, since it does not require the elevated temperatures necessary in ordinary vulcanisation, during which there is a considerable deterioration in the properties of the ion-exchange resins present in the membranes.

The radiochemical method can be used to prepare membranes which do not contain ion-exchange groups but which nevertheless exhibit extremely important properties. Thus the radiochemical cross-linking of poly(vinyl alcohol) or a mixture of poly(vinyl alcohol) with bifunctional monomers makes it possible to prepare chemically pure membranes, which may find application in biochemical processes[89].

The above data show that ion-exchange membranes prepared under the influence of radiation differ from ordinary membranes in their more uniform composition, increased thermal and chemical resistance, high mechanical strength, low electrical resistivity, increased selectivity, etc. Similar conclusions have been reached by others[90-94].

2. RESINS

Ionising radiation is used much less frequently in the preparation of ion-exchange resins than in the preparation of ion-exchange membranes, but the use of radiation in this field is fairly promising and makes it possible to obtain ion-exchange resins with improved physicochemical and physicomechanical properties.

One of the main stages in the preparation of polymerisation ion-exchange resins—the copolymerisation—can be effectively initiated by ionising radiation. This is true primarily of suspension (drop) copolymerisation, in which ion-exchange resins with regular spherical shape and almost any particle size from 1 μm to 2 mm can be obtained. Suspension copolymerisation under the influence of ionising radiation has the following advantages over the methods usually employed.

1. The copolymerisation can be carried out at room temperature and below, and this improves the conditions of heat transfer, improves the physicomechanical and physicochemical properties of the copolymer, decreases the probability of adhesion of the granules, and improves the stability of the suspensions. Radiation copolymers of styrene and divinylbenzene have greater mechanical strength and thermal stability than the ordinary copolymers[95]. Thus for a divinylbenzene content of up to 10 wt. %, the breaking stress for a copolymer prepared by irradiation amounts to 700 kgf cm^{-2}, whereas that for the ordinary copolymer is not more than 490 kgf cm^{-2}. The degradation temperature of the copolymer obtained by irradiation is 23 deg higher than that of the ordinary copolymer. Both types of copolymer show a decrease in breaking strength with increase in the divinylbenzene content above 10%, but the decrease is much less marked for the copolymer prepared by irradiation.

2. The absence of copolymerisation initiator from the system makes it possible to obtain copolymers with a high degree of purity. The use of ionising radiation makes it possible to reduce the number of components in the complex reaction mixture, which, in addition to monomers, usually contains initiators, stabilisers, and other substances which make it difficult to isolate the resulting copolymers in pure form[96,97]. This is particularly important in the preparation of nuclear grade resins[98-101] and

‡ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

resins for analytical purposes[101], which should differ from ordinary standard ion-exchange resins by having a high degree of purity. For example, in nuclear grade resins the percentage concentration of impurities should not exceed the following values: iron 5×10^{-3}, copper 10^{-3}, and lead 10^{-4}.[101] Resins for analytical purposes must satisfy even stricter requirements; the percentage concentration of impurities should not exceed the following values: iron 10^{-4}, copper 8×10^{-5}, nickel 5×10^{-6}, lead 2×10^{-5}, and aluminium 1.5×10^{-3}; the total ash content should not exceed 4×10^{-2}%.[101]

3. Other conditions being equal, the maximal degree of conversion is greater when ionsing radiation is used than when chemical initiators are used, apparently due to an increase in the mobility of the macromolecular segments under the influence of radiation[102]. This feature is particularly important when the reaction mixture contains an appreciable (> 10–15%) quantity of cross-linking agent, for example, in the preparation of non-swelling macroporous resins, where in chemical methods of preparation ~ 20–30% divinylbenzene takes part in the copolymerisation for only one double bond[103].

Resins with a highly developed specific surface can be prepared under the influence of ionising radiation. For example, macroporous copolymers can be obtained by carrying out the radiation copolymerisation of styrene and divinylbenzene in granules of silica gel, which is then removed by dissolving it in concentrated alkali solution. This method of preparation makes it unnecessary to introduce into the reaction mixture the foaming agents or inert solvents which are usually employed in the preparation of macroporous ion-exchange resins[101–107]. In addition to silica gel, it is also possible to use other porous matrices whose chemical decomposition can be carried out fairly simply.

Since in many polymers irradiation leads to intensive cross-linking, it is sometimes possible to use irradiation instead of cross-linking agents. For example, linear buadiene–styrene copolymer is converted into a three-dimensional insoluble product by treatment with ^{60}Co γ-radiation (dose about 10 Mrad). Subsequent sulphonation of the resulting three-dimensional polymer with concentrated sulphuric acid leads to the formation of a strongly acidic cation-exchange resin[86]. It should of course be borne in mind that this cross-linking is effective for systems with a fairly high value of $G_{\text{cross-linking}}$. For systems with a low value of $G_{\text{cross-linking}}$, however, the doses required to obtain the necessary number of cross-linkages are too large. Thus the formation of the same number of cross-linkages as are present in a copolymer of styrene with 4% divinylbenzene requires irradiation of polystyrene with a dose of ~ 10 000 Mrad, and this is quite unacceptable.

The use of ionising radiation in the production of ion-exchange resins is not limited to the copolymerisation stage. In a number of instances irradiation produces various desirable properties in previously prepared resins. This is true primarily of sulphonic acid cation-exchange resins, whose functional groups are fairly stable towards radiation[108]. For example, specimens of the resins Dowex-50 (2–24% divinylbenzene) and Amberlite IR-120 (8% divinylbenzene), irradiated with ^{60}Co γ-radiation (dose 10–450 Mrad; dose rate 550 rad s^{-1}), were found to be much more stable towards hydrolysis at high temperatures than the original specimens. Non-irradiated ion-exchange resins at 180°C lost 25–30% sulphur and became almost completely soluble, whereas the stability of the resins towards hydrolysis under these conditions increased considerably after irradiation and the loss of sulphur was reduced to 10–15%.[109]

Irradiation has a definite influence on the selectivity of the sorption of various ions[108]. This feature can also be of some practical importance. For example, irradiated KU-2 resin shows an increase in selectivity for the caesium ion in the exchange of H^+ by Cs^+.[110] An analogous phenomenon was observed for the sorption of organic compounds, for example, phenol[111,112].

3. FIBRES, FABRICS, PAPER

Ion-exchange fibres and fabrics have recently become fairly widespread[113,114]. These materials can operate simultaneously as mechanical and ion-exchange filters. They are particularly promising for the technological development of continuous countercurrent processes[115]. Ion-exchange textiles show a combination of properties which sometimes makes them superior to ordinary resins[116]. They have a more highly developed surface than granulated resins, as a result of which ion-exchange processes take place at high rates on these materials. The use of ion-exchange fabrics makes it possible to carry out ion exchange on small-scale equipment of the filter-press type. This makes it possible to remove ions from a pulp and to carry out mechanical filtration, and this is almost impossible on ion-exchange columns. Ion-exchange fabrics can be used for the preparation of the framework of heterogeneous membranes.

The radiochemical method for preparing these materials is apparently more effective than other methods of preparation. The grafting of acrylic and methacrylic acids, methyl methacrylate and acrylonitrile (with subsequent hydrolysis), 4-vinylpyridine and 2-methyl-5-vinylpyridine (with subsequent alkylation), styrene (with subsequent sulphonation or amination) and various other monomers from the liquid or gaseous phase on to polyethylene, polypropylene, poly(tetrafluoroethylene), poly(vinyl chloride), poly(ethylene terephthalate), cellulose, and other fibres not only gives the fibres and fabrics ion-exchange properties but also in a number of instances leads to a marked improvement in their mechanical strength and thermal stability[33]. Grafting on to fibres usually takes place with high radiochemical yields; even at doses of 1–2 Mrad, the quantity of polymer grafted amounts to several dozen percent, and this gives fabrics with a total exchange capacity of 1–5 mg-equiv. g^{-1}.[117,118]

Fibres exhibiting weakly acidic or weakly basic properties are obtained by irradiating polyethylene and polypropylene fibres in air at room temperature and then heating with acrylic acid or 2-methyl-5-vinylpyridine. The total exchange capacity of fibres containing 40–50 wt.% graft polymers amounts to 2–3 mg-equiv. g^{-1}. The presence, in the fibres, of antioxidants of the substituted phenol and aromatic amine type decreases the efficiency of grafting[118].

The grafting of acrylic acid or acrylonitrile (followed by treatment with alkali) on to polypropylene fibres gives fibres with an exchange capacity in neutral solution up to 4 mg-equiv. g^{-1}.[74]

Ion-exchange fibres and fabrics can be prepared by surface grafting, whereas with ion-exchange membranes the grafting should take place throughout the entire volume of the irradiated polymer.

Cellulosic ion-exchange materials containing functional groups, in particular various papers, can be used successfully in analysis, particularly for the chromatography of biochemical materials: proteins, enzymes, nucleic acids, etc.[119]

Ion-exchange papers and fibres can be obtained by the radiation grafting of various monomers, containing ion-exchange groups, on to cellulose, or by the subsequent introduction of these groups into the graft copolymer. The radiochemical preparation of ion-exchange materials based on cellulose, however, is of much less practical importance than that based on synthetic fibres. This is due to the fact that the introduction of a comparatively small quantity of ion-exchange groups (1–2 mg-equiv. g^{-1}) into cellulose leads to a sharp increase in its ability to undergo swelling and to a deterioration in the physicomechanical properties. Moreover, the grafting of various vinyl monomers on to cellulose can hardly give sorbents with advantages over ordinary ion-exchange celluloses.

The radiation grafting of styrene on to cellulose under the influence of γ-radiation, followed by the introduction of ion-exchange groups into the graft polymer, makes it possible to obtain ion-exchange paper with a greater stability towards radiation than the original cellulose[120]. Thus on irradiation with a dose of ~ 50 Mrad, the tensile strength of pure cellulose decreases by 83%, whereas the corresponding figure for a copolymer containing ~ 35 wt.% graft polystyrene is only 47%.[121] When hydrophobic polymers such as polystyrene or poly(methyl methacrylate) (in quantities greater than 13–20 wt.%) are grafted on to cellulose, there is a marked change in the Rf values, the times required for separation, and the form of the spots in the molecular chromatography of aliphatic acids and dyes[120]. Ion-exchange papers can be prepared from materials other than cellulosic materials. For example, the grafting of acrylonitrile and acrylic acid on to polypropylene fibres under the influence of ^{60}Co γ-radiation makes it possible to obtain cation-exchange papers with a thickness of 0.2 mm, a capacity of 4 mg-equiv. g^{-1}, and a resistivity of 12 Ω cm (in 1 N NaCl)[74].

4. MINERAL-ORGANIC SORBENTS§

A number of ion-exchange materials consisting of an inorganic carrier-support and an organic fraction containing various functional groups capable of ion exchange have recently been prepared. These materials have certain advantages over ordinary ion-exchange resins. They show an increased thermal and radiochemical stability, a high rate of attainment of ion-exchange equilibrium, a low degree of swelling in the working solutions, and the ability to act as mechanical filters. The disadvantages of most of these materials generally include poor chemical stability and a lower exchange capacity on a weight basis than ordinary ion-exchange resins.

The mineral-organic products on which the subsequent preparation of the ion exchangers is based may be obtained by chemical[122,123] or chemical and mechanical[124] methods¶. For example, cation exchangers with capacities up to 0.5 mg-equiv. g^{-1} have been prepared by condensing dibenzyldichlorosilane with the hydroxyl groups of silica gel or aerosil and then sulphonating the products[125]. Cation exchangers with a capacity of 1 mg-equiv. g^{-1}, which are stable at 300°C and have found application as catalysts, have been prepared from silica gel and sulphonated benzyltrichlorosilane[126]. The reaction of silica gel with various aminosilanes gives anion exchangers with capacities up to 0.8 mg-equiv. g^{-1}, stable at temperatures above 200°C.[127]

The most universal method for the preparation of mineral-organic products, however, is the radiochemical method. It can be used for grafting on to surfaces which do not contain groups capable of undergoing condensation. It does not require mechanical subdivision and makes it possible to carry out grafting on highly dispersed materials. Finally, the radiochemical method can be used to obtain products with a high concentration of organic fraction, whereas this is generally difficult or impossible by chemical or chemical-mechanical methods.

Mineral-organic ion exchangers have been prepared by radiochemical vapour-phase graft polymerisation[10,128-131]. The mineral-organic products were made in the apparatus illustrated in Fig. 2. The inorganic carrier-support was placed in a thin-walled glass ampoule (*1*), and the liquid monomer was placed in the flask (*2*). The ampoule was separated from the flask by the glass filter (*3*). The apparatus was evacuated to a residual pressure of 10^{-5}–10^{-6} mmHg and sealed off. The ampoule was placed in the air thermostat (*4*) fitted with a window of thin aluminium foil (*5*) to permit irradiation. The flask containing the monomer was immersed in the water or oil thermostat (*6*), in which a temperature determined by the vapour pressure of the monomer in the system was maintained. The apparatus was rotated by means of a small motor (*7*). After irradiation by X-rays or a beam of accelerated electrons, the apparatus was opened and the homopolymer was separated from the mineral-organic product by extraction with a suitable solvent. The quantity of graft polymer usually amounted to 10–20 wt.%. When the graft polymer contained functional groups capable of ion exchange—for example, poly(acrylic acid)—the mineral-organic ion exchanger was obtained in a single stage. Otherwise, the functional groups were introduced into the graft polymer by further chemical reactions. Graft polystyrene was sulphonated or aminated, graft poly(4-vinylpyridine) was alkylated, and poly(vinylphosphonic dichloride) was hydrolysed with water. The following mineral-organic ion exchangers were prepared in this way: macroporous silica gel–sulphonated polystyrene; macroporous silica gel–aminated polystyrene; macroporous silica gel–alkylated poly(4-vinylpyridine); macroporous glass fibre–alkylated poly(4-vinylpyridine); "white soot" [powdered silica gel (Ed. of Translation)] (or aerosil)–sulphonated polystyrene;

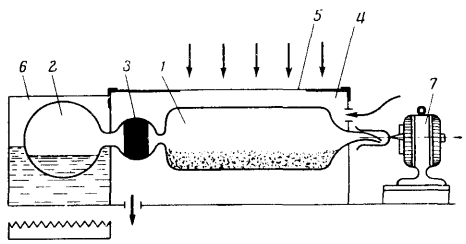


Fig. 2. Apparatus for vapour-phase radiochemical graft polymerisation[29].

§ Since these sorbents are based on synthetic inorganic materials, it would be more correct to call them inorganic-organic sorbents.

¶ Methods for the preparation of mineral-organic products have been reviewed in detail by Morozov[34].

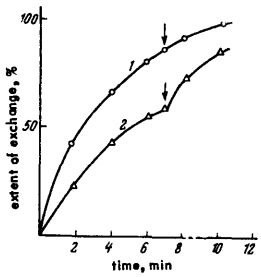
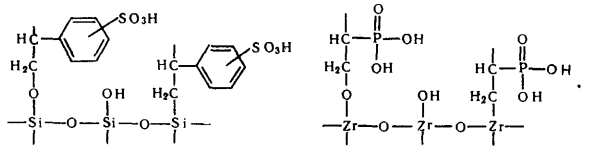


Fig. 3. Rate of exchange of H^+ by Cs^+:[130] 1) for a mineral-organic ion exchanger (macroporous silica gel–sulphonated polystyrene); 2) for KU-2-6 resin. The arrows mark the points at which the sorbents were removed from the solutions for 12 h.

"white soot" (or aerosil)–poly(acrylic acid); and zirconium oxide–poly(vinylphosphonic acid). The suggested structures of mineral-organic sorbents of the macroporous silica gel–sulphonated polystyrene and zirconium oxide–poly(vinylphosphonic acid) types are given below:



The ion exchangers obtained have a capacity of 1–2 mg-equiv. g^{-1} in neutral solutions, undergo slight swelling in water (5–10%), and have a highly developed specific surface, varying from several dozen to several hundred square metres per gramme. Most of them can also be used as mechanical filters. The rate of attainment of ion-exchange equilibrium in these ion exchangers is usually not limited by internal (gel) diffusion, as in ordinary resins (Fig. 3). The rate is very high even in dilute solutions. Thus the half-saturation time (the time required for 50% of the capacity of the resin to be realised) in the exchange of H^+ by Na^+ in 2×10^{-4} N NaCl amounts to only a few minutes for mineral-organic ion exchangers, compared with 30–40 min for KU-2-6 resin. Mineral-organic ion exchangers also have a high radiochemical stability. Thus an ion exchanger based on the system formed by macroporous silica gel with polystyrene containing $-CH_2N^+(CH_3)_3$ groups loses only 40% of its capacity on irradiation in water with a dose of 500 Mrad, whereas AV-17 anion-exchange resin†, which contains analogous groups, loses its ion-exchange properties completely under the same dose[132].

Finally, various mineral-organic ion exchangers show a high heat resistance, retaining their ion-exchange properties up to 300°C.

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THE USE OF GAS CHROMATOGRAPHY IN THE STUDY OF POLYMERS

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Chromatography is a physical method for the separation of compounds, in which the substances being separated are distributed between two phases, one of which is stationary,

while the other is mobile and filters through a layer of the stationary phase[1,2].

Gas chromatography is a form of chromatography in which the mobile phase is a gas. In a gas-chromatographic separation, the molecules of a compound being analysed are moved by a stream of carrier gas, so that gas chromatography can be used for the separation of only those compounds which can be transported without decomposition in the gaseous state. Thus the gas-chromatographic method cannot be used directly to separate non-volatile macromolecular compounds, and its application is restricted to volatile compounds with vapour pressures not less than several mmHg at the temperature of the separation. Accordingly, gas chromatography is used to determine the concentration of volatile products in polymers, or in compositions based on them. A common feature of these methods is that the polymer is introduced into the chromatography either in suspension or in solution in a suitable solvent. To facilitate calculations, a standard is usually added to the mixture introduced into the chromatograph. The polymer is retained in the column (a special short initial column, which is replaced at intervals, is often used to separate the polymer) and the solvent, standard, and volatile impurities present in the polymer are separated and detected.

A method has been developed for determining residual monomer and other volatile components in polymers based on styrene[3]. Dimethylformamide is used as solvent, and toluene is used as standard. The volume of sample taken is 5 μl. The sensitivity of the method corresponds to 10^{-6} g monomer in 1 g polymer.

Wilkinson and coworkers[4] developed a method for determining residual monomers in latices. Acetic anhydride, 2,2-dimethoxypropane, and cyclohexanone can be used as solvents. The first two solvents react with water and convert it into other compounds more convenient for chromatographic study. A separate initial column containing glass wool is used to separate the latex. The volume of sample used is 0.02–0.1 ml. The sensitivity is 0.01–0.05%.

A method has also been developed for determining free phenol and formaldehyde in phenolic resins[5].

Gratsianskaya and coworkers[6] were the first to use an analogous method for the quantitative determination of polymeric substances in a reaction system, for the example of the isomerisation of α-pinene into camphene, during which polymeric ompounds are also formed. A short initial column was used to separate the polymers. Cineol and menthol were used as internal standard. The concentration of polymer was determined from a comparison of the percentage concentration of standard in the prepared mixture and that determined by chromatographic analysis.

The application of gas chromatography to the direct study of polymers is possible only with a new type of approach, since the classical version of the analysis is impossible for non-volatile substances. In the study of polymers and other non-volatile compounds by gas chromatography, two approaches are possible in principle: (1) analysis of the polymers by the recently proposed method of "reversed" gas chromatography, and (2) analysis of macromolecular compounds from the products of chemical changes.

In the new method of "reversed" gas chromatography, in contrast to the usual version, the unknown system is the stationary liquid phase, on which known volatile compounds are separated[7]. The organic compounds used as stationary liquid phases are characterised by a definite spectrum of relative retention times for standard compounds. The spectra of the standard compounds change markedly with change in the nature of the stationary phase. Polymers can also be used as unknown stationary liquid phase; this can be used, in particular, to characterise their molecular weights. If the molecules of the polymer contain functional terminal groups differing from the main chain, there should be a definite relationship between the concentration of these groups (and hence the molecular weight of the polymer) and the retention times for standard compounds. This relationship for polyethyleneglycol maleate adipate[8] is given in Fig. 1.

The method of "reversed" gas chromatography can also be used to study phase changes in polymers, for example in polyethylene[9]. In the region of a phase change (fusion) the curves giving the dependence of the retention time or peak width on the column temperature show a maximum due to the change in the distribution constant resulting from the phase change (Fig. 2).

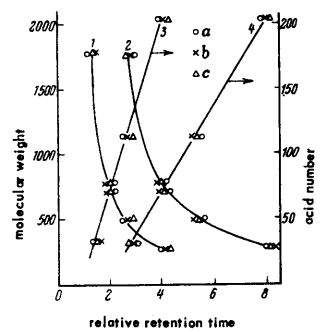


Fig. 1. Dependence of the relative retention times of ethanol (1, 3) and propanol (2, 4) on the number-average molecular weight and acid number of polyethyleneglycol maleate adipate; *a*), *b*), *c*) series of experiments.

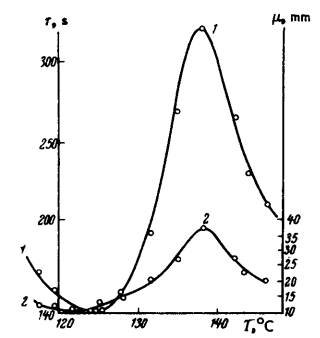


Fig. 2. Dependence of the retention time (1) and peak width (2) of n-tetradecane on the temperature of the column. The stationary phase is a mechanical mixture of polyethylene (1%) and glass beads.

The method of "reversed" gas chromatography can apparently also be used to determine the structure of polymers, the composition of copolymers, and other polymer characteristics which influence the change in the "gas–liquid" distribution constants for standard volatile compounds. An advantage of the method is that it makes possible the direct study of a polymer (without decomposing it) in small samples, but one restriction is the viscosity of the compounds being studied, which should not be too great at the temperature of the experiment[10]. "Reversed" gas chromatography can also be used to study the kinetics of chemical reactions[11], including polycondensation.

A method more widely used at present in the study of polymers characterises macromolecular substances by an indirect method—the macromolecular compound is characterised by the spectrum of volatile products formed by chemical changes. Here we must first mention the extensive application of the universal reaction of pyrolysis in the study of polymers, since the use of other chemical methods is often limited by the chemical inertness, the absence of functional groups, and the insolubility of many polymers of practical importance.

Disadvantages of the pyrolysis method include the complexity of the chemical reactions taking place during thermal degradation and the generally important part played by secondary reactions. The processes involved in the thermal degradation of polymers have as yet been insufficiently studied. Thus in general it is impossible to predict quantitatively the spectrum of volatile products from a knowledge of the structure and conditions of pyrolysis of the polymer; the opposite problem (the determination of the structure and composition of a polymer from the pyrolysis products), which is of considerable analytical interest, has not yet been solved theoretically.

The analyst's task is to establish an empirical correlation between the structure of a polymer and the spectrum of the products formed on pyrolysis. Since the composition of the pyrolysis products is determined by many factors (temperature, duration of pyrolysis, size of sample, etc.), the dependence on the structure of a polymer of the composition of the pyrolysis products becomes unambiguous only with strict standardisation of the conditions of pyrolysis, including some standardisation of the sample.

Thermal degradation followed by analysis of the degradation products has for long been used for the qualitative and quantitative analysis of macromolecular compounds and to establish their structures[12–15]. The use of the gas-chromatographic method for the analysis of the products has greatly increased the value of this method in the study of polymers, since in the complex mixture of products formed, only a few are characteristic of a given type of polymer. Thus for the analysis of volatile compounds, gas chromatography is in general a more selective method than spectroscopy and a simpler method than mass spectroscopy.

The use of gas chromatography for the analysis of pyrolysis products is due to the following fundamental advantages of gas chromatography as an analytical method: (1) the use of sensitive detectors makes it possible to carry out the analysis with small polymer samples of the order of one milligramme or several tens of microgrammes; (2) the high efficiency of separation on packed columns—1–3 thousand theoretical plates (t.p.)—or in capillary columns (20–60 thousand t.p.); (3) the time required for the analysis is short and usually varies from several minutes to several tens of minutes; and (4) standard chromatographic apparatus is used for the separation, and the pyrolysis unit consists of a small independent attachment fo the standard chromatograph.

The method of studying non-volatile compounds from the chromatographic spectrum of the volatile products is often called pyrolytic gas chromatography.

In the earliest work on the use of gas chromatography for the analysis of polymer degradation products[16–18], the pyrolysis was carried out in a special assembly, and the products were removed and analysed on a standard gas chromatograph. This method is convenient when the use of small samples (about 1–10 μg) is impossible because of the inhomogeneity of the specimen, to study the mechanism and kinetics of pyrolysis, to estimate the heat resistance of a material, when it is necessary to study the composition of the products at low degrees of conversion, etc.[19]

In a second version, the pyrolysis and the chromatographic separation are combined in a single instrument. This method for studying polymers by pyrolysis of a specimen in a special reaction vessel in front of the gas-chromatographic column in a current of carrier gas was first described by Lehrle and Robb[20]. This method has the following advantages: (1) the time required for the study is reduced considerably, since the pyrolysis and introduction of the sample are combined in a single short operation; (2) the study requires only small quantities of specimen (of the order of several milligrammes or even microgrammes); (3) for small samples (thin layers) the part played by secondary reactions is reduced; and (4) it is possible to carry out the pyrolysis under reproducible controlled conditions and to analyse both liquid and gaseous products.

An interesting intermediate version of the pyrolytic method was proposed by Swann and Dux[21]. The pyrolysis of the polymer being studied was carried out in an evacuated glass ampoule (weight of specimen 50 mg, duration of heating 15 min). The pyrolysis products were studied by gas chromatography; the ampoule was broken in a current of carrier gas in front of the column inlet.

An analogous method was used successfully for the quantitative determination of hydroxyethyl groups in hydroxyethyl–starch[22]. A sample of the substance being studied (0.001 g) was pyrolysed in a sealed capillary (9.0 × 0.1 cm) in a vacuum at 400°C for 10 min. The pyrolysis products were studied chromatographically. It was established that there is a linear relationship between the height of the acetaldehyde peak and the quantity of hydroxyethyl groups in the specimen being analysed.

A more widespread version of the pyrolytic method is that in which the cell for the pyrolysis is also the assembly for the introduction of the sample into the chromatographic column.

The layout of the apparatus in pyrolytic gas chromatography is characterised by considerable variety; the pyrolysis cells designed by foreign firms are extremely varied. The various pyrolysis cells can be divided into two design types. In pyrolytic reactors of the first type, the pyrolysis is carried out on a filament (spiral), which is heated rapidly by electric current. The heated spiral is placed in a flow chamber whose walls are at a temperature not exceeding the temperature of the subsequent chromatographic separation.

When these cells are used, the substance being studied is applied to the metallic filament (usually platinum or Nichrome). The spiral carrying the substance to be analysed is then placed in the gas stream, the cell is made airtight, the instrument is brought to operating conditions, and the spiral is heated. The resulting pyrolysis products are carried by the carrier gas into the chromatographic column, separated, and recorded by the detector. With cells of this type the design is simple, the specimen being studied can be heated rapidly to the required temperature, the pyrolysis is carried out in a stream of carrier gas, and the heating surface is small, so that the possibility of secondary reactions by the pyrolysis products is reduced. Cells of this type must satisfy the following requirements: (1) the cell colume must be as small as possible, since increase in its volume leads to a decrease in the efficiency of the subsequent chromatographic separation; (2) supplementary heating of the cell walls is required to prevent condensation of liquid pyrolysis products on the cold walls of the cell; alternatively, the cell can be placed in a thermostat; and (3) rapid and convenient replacement of the spirals carrying the substance being studied must be possible. Pyrolysis cells of this type can be used to carry out pyrolysis in various gaseous media, including reactive media, or in a vacuum.

The construction of a typical glass pyrolytic cell[23] is illustrated in Fig. 3. Cells of similar design are described by Janak[24], Jones and Moyles[25,26], and Mljenek[27]. These authors used chromatographs with an ionisation detector, since the total volume of products formed by pyrolysis on the spiral from very small samples is insufficient for detection by the simpler but less sensitive katharometer.

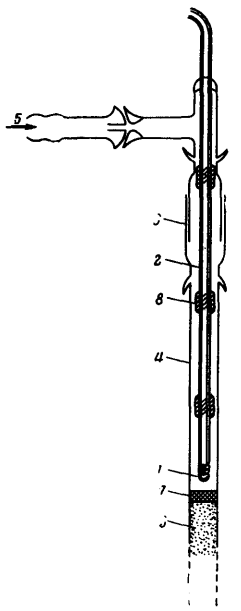


Fig.3. Glass cell for pyrolysis:
1) Nichrome spiral (0.2 Ω); 2) tungsten electrodes (diameter 1 mm); 3) sorbent; 4) column; 5) carrier gas inlet; 6) ground joint; 7) layer of asbestos; 8) glass insulation.

Franc and Blaha[28] worked with a pyrolysis cell in which platinum gauze was used instead of a spiral. This made it possible to increase the quantity of specimen being analysed, without increasing the weight of polymer per unit area of wire, so that it became possible to detect the pyrolysis products by means of a katharometer.

The temperature of the cell does not remain constant during the pyrolysis; Fig. 4 shows the change in the temperature of the cell and the concentration of volatile products with time in various experiments on the pyrolysis of a poly(propene oxide–tetrahydrofuran) copolymer. Thus the pyrolysis of the polymer actually takes place under conditions of rapidly changing temperature.

Kyryacos and coworkers[29] suggested the application of a higher voltage to the spiral at the start of pyrolysis in order to reduce the time required to heat the spiral to a given temperature.

The use of metallic filaments and spirals (platinum, Nichrome, etc.) as supports for the polymer film during pyrolysis is not the best arrangement, because of the possible catalytic activity of the metals. It has been shown[26] that for samples weighing more than one milligramme the filament material has a marked influence on the spectrum of products; the spectrum of pyrolysis products is simpler when a gold-plated filament is used than when a Nichrome filament is used. When smaller samples (20–30 μg) are used, however, the spectrum of pyrolysis products for polystyrene and poly(methyl methacrylate) are independent of the spiral material (Nichrome, platinum, gold-plated platinum). This undesirable factor for large samples can apparently be eliminated by using glass coated filaments.

It is sometimes convenient to place the sample for pyrolysis in a small boat of mica, quartz, or other more inert material, instead of directly on the spiral[30].

It has been reported[30] that when the pyrolysis of rubbers is carried out in a small mica boat heated with a Nichrome spiral, the gas-chromatographic spectra of the products are more characteristic (that is, greater differences are observed between them) than when the sample for pyrolysis is deposited directly on the spiral.

A method has also been described for studying non-volatile organic compounds by pyrolysis of a weighed specimen of the substance (5–30 μg) placed in a capillary

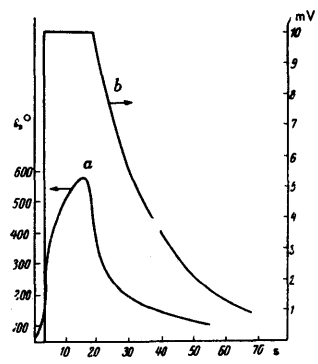


Fig.4. Change in the temperature of the spiral (*a*) and the concentration of volatile products (*b*) during pyrolysis.

(0.2 × 0.05 cm) sealed at one end[31]. The area and height of the peak were found to be linearly dependent on the size of the sample.

In pyrolysis cells of the second type, the specimen for pyrolysis is introduced into a high-temperature zone of a tubular reactor, where the thermal degradation takes place. An advantage of reactors of this type is the more effective standardisation of the thermal conditions, but a disadvantage is the possibility of secondary reactions by the pyrolysis products as a result of the increased time for which they are present in the hot zone.

Increase in the dimensions of the polymer sample being analysed makes it possible to supplement the gas-chromatographic method for the study of the degradation products with other physicochemical methods for the analysis of the residues from the pyrolysed polymer (chemical, spectroscopic, etc.).

Various methods for heating the specimen for pyrolysis have been described: (1) introduction of the small boat into a hot zone, heated to a high temperature[32]; (2) the use of an electric heater consisting of a platinum wire wound directly on to the boat or capillary[33,34]; (3) immersion of a U-shaped vessel containing the specimen in a bath of Wood's alloy (500–550°C);[35] and (4) induction heating of the specimen, mixed with a metal powder, by high-frequency currents[36].

An original assembly for the pyrolysis of polymers was proposed by Giacobbo and Simon[37,38]. The specimen for pyrolysis is deposited on a wire of ferromagnetic material (0.5 × 20 mm) and placed in a glass capillary in the stream of carrier gas. The ferromagnetic wire is heated rapidly to the Curie point in ~ 2×10^{-3} s by means of a high-frequency furnace. During pyrolysis of the polymer, the temperature of the wire remains constant at the Curie point. The temperature of pyrolysis can be varied to some extent by using different ferromagnetic materials. The method has been used to study the spectra of pyrolysis products from various amino-acids. This method of heating the specimen for pyrolysis was also used by Völlmin and coworkers[39].

Reactors using a heated filament have found wider practical application.

To obtain reproducible results and a characteristic spectrum of pyrolysis products, it is necessary to select the optimal parameters for the experiment, and these should be standardised precisely.

The thermal degradation of a polymer is sensitive to even slight changes in the conditions of pyrolysis. The decisive parameters in the rational design of a cell are as follows: (1) the size and geometric form of the specimen for pyrolysis; (2) the temperature conditions of the pyrolysis; (3) the duration of pyrolysis; and (4) the conditions of the chromatographic separation.

The polymer is deposited on the spiral of the pyrolysis cell by two main methods: (1) from solution by evaporation (for soluble substances) or from a suspension (for insoluble substances); and (2) small specimens (several milligrammes) of identical shape are placed directly inside the spiral.

A film can be obtained by immersing the spiral or filament in a dilute solution or suspension; Alternatively, a solution or suspension containing ~ 1 wt.% of polymer can be applied by means of a soft brush to one or two rings in the centre of the spiral, which is then dried; the drying can be accelerated using an infrared lamp[25].

Sometimes, the specimens for pyrolysis are first finely divided, and plasticisers and other soluble substances are removed by extraction[40]. It is sometimes recommended that the sample be deposited on the wire from alkaline or acidic solutions[38,41].

The removal of solvent and other volatile substances (gases, monomers, moisture, etc. dissolved in the polymers) can apparently be carried out conveniently by heating the polymer, before pyrolysis, at a temperature lower than that at which degradation begins.

In the study of the mechanism of pyrolysis, and sometimes in the study of the fine structural details of a polymer, the more complicated method of thin films is apparently the optimal method, since in thick films the low rate of diffusion, the increase in the part played by secondary reactions, and a number of other factors lead to distortion of the true rate of the process and a change in the qualitative composition of the pyrolysis products[25,42].

Jones and Moyles[26], in a study of the dependence of the composition of pyrolysis products on the size of the sample, demonstrated the advantages of working with small microgramme specimens. They give for comparison two chromatograms, obtained using milligramme and microgramme specimens of styrene homopolymer. The pyrolysis conditions were the same in both cases. The appearance of additional peaks on the chromatogram of the degradation products for the milligramme specimen indicates that the part played by secondary reactions is greater when large specimens are used. Since it is difficult in practice to obtain such a thin film, the degradation is usually carried out on thicker films, with the same thickness in all experiments. According to Voight[42,43], fluctuations of ±50% in the weight of sample produce no significant changes in the chromatographic spectrum of the pyrolysis products.

The structures of various amino-acids were investigated by pyrolysis of thin films of the acids[39]. The pyrolysis products were separated on capillary columns, and detected using a mass spectrometer fitted with a rapid scanning device.

A problem of practical importance concerns the possibility of applying the pyrolytic method to specimens which contain other components in addition to the polymer itself. When the polymer is insoluble in water and the other components soluble, it might be possible to prepare aqueous emulsions or suspensions of these specimens and to deposit them on a spiral and examine them in the usual way. The possibility of carrying out the direct study of industrial specimens was demonstrated by Jones and Moyles[26], who obtained identical chromatograms for the pyrolysis products from a specimen of pure polymer and a specimen containing various inert fillers. The polymer powder was mixed with the natural resin tragacanth (1 wt.%) and water, and applied to the filament in the form of a suspension for subsequent pyrolysis.

The pyrolysis may also be influenced by the carrier gas velocity, which determines the duration of contact between the pyrolysis products and the high-temperature spiral. It has been reported[44] that a decrease in the carrier gas velocity from 60 ml min^{-1} to 40 ml min^{-1} doubled the concentration of benzene in the products of the pyrolysis of polystyrene.

This effect is not always observed, however. Thus in the pyrolysis of atactic polypropylene in the range 320–935°C, the quantity of products did not change with change in the carrier gas velocity[45].

In the study of the structure of a polymer, the pyrolysis conditions should be chosen in such a way that the spectrum of polymer pyrolysis products obtained characterises unambiguously the material subjected to pyrolysis. To satisfy this requirement, it is apparently necessary that the final products be produced as a result of the minimal number of changes, that is, they should have a short "genealogy". It is then obviously easier to follow the relationship between the products of the change and the structure of the specimen being studied.

To reduce the part played by secondary reactions in the formation of the pyrolysis products, the temperatures used are usually not too high (400–800°C) and the time for which the products remain in the hot reaction zone is reduced.

An increase in the number of polystyrene pyrolysis products with increase in the temperature of pyrolysis has been demonstrated[44].

The optimal temperature of pyrolysis is determined by the nature of the analytical problem, the type of polymer studied, and the design of the pyrolysis cell. For example, in the determination of the monomeric composition of a copolymer, the optimal temperature is the temperature at which the relative yield of characteristic pyrolysis product varies most rapidly with change in the composition of the copolymer. The dependence of the percentage yield of methyl acrylate on the potential difference applied to the spiral (the voltage applied to the spiral determines its temperature) for copolymers of methyl methacrylate and methyl acrylate[46] is shown in Fig. 5.

The nature of the carrier gas also determines the conditions of pyrolysis to an appreciable extent. In the pyrolysis of atactic polypropylene, the temperature at which the gaseous pyrolysis products are liberated is about 200 deg higher in an atmosphere of nitrogen than in an atmosphere of hydrogen[47].

In the selection of conditions for the chromatographic separation, allowance must be made for the nature of the pyrolysis products. In the study of the composition of the pyrolysis products from hydrocarbon polymers, it is best to use non-polar phases, but in the study of hetero-atomic compounds it is best to use polar phases. In the analysis of volatile pyrolysis products, it is apparently best to use simultaneously two or three standard chromatographic columns containing phases with different polarities. In view of the wide range of boiling points among the pyrolysis products and also the complexity of the qualitative composition of the products, it is desirable, particularly in the study of the mechanism of thermal degradation, to use capillary columns combined with temperature programming[48]. A combination of pyrolysis in a vacuum and pyrolysis in contact with air has been used to determine the mechanism of the degradation of polystyrene and to identify the pyrolysis products in the range 300–420°C.[49]

It is convenient to express the results of the chromatographic analysis of the pyrolysis products in relative units, using the internal standard method, that is, in the form of line diagrams on coordinates S_i/S_{st} against $\lg(t_i/t_{st})$, where S_i and S_{st} are the areas of the peaks of the ith compound and the standard, and t_i and t_{st} the retention times of the ith compound and the standard. When the results are expressed in this form, it is possible to smooth out the changes due to fluctuations in the dimensions and weights of the specimens, the carrier gas velocities, temperature, etc.[30] Pyrograms obtained for various sample weights and various carrier gas velocities are given in Fig. 6. All these outwardly different pyrograms correspond to the same line diagram.

A large amount of factual material has now been obtained from the study of a wide variety of polymeric materials and non-volatile organic compounds by pyrolytic gas chromatography: Nitrocellulose, α-butyl methacrylate, poly(vinyl alcohol), poly(vinyl chloride), poly(methyl methacrylate),

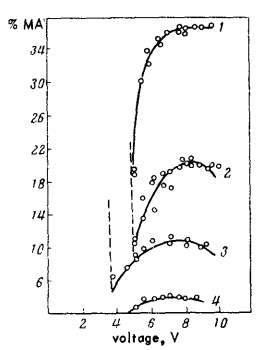


Fig.5. Dependence of the yield of methyl acrylate on the potential difference applied to the spiral for the pyrolysis of methyl methacrylate (MMA)–methyl acrylate (MA) copolymers. Polymer composition: 1) MMA : MA = 1 : 3; 2) MMA : MA = 1 : 1; 3) MMA : MA = 3 : 1; 4) MMA : MA = 9 : 1.

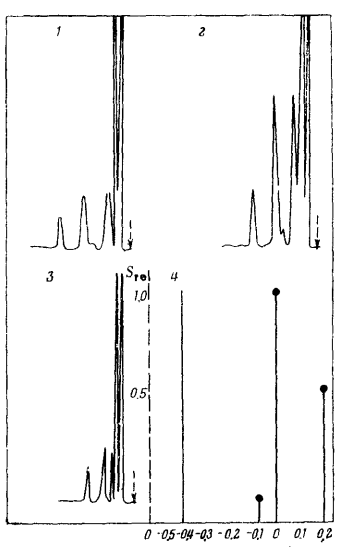


Fig.6. The use of line diagrams in pyrolytic gas chromatography: 1) pyrogram for 2.3 mg polymer specimen, carrier gas velocity 30 ml min^{-1}; 2) pyrogram for 4.6 mg polymer specimen, carrier gas velocity 30 ml min^{-1}; 3) pyrogram for 2.3 mg polymer specimen, carrier gas velocity 50 ml min^{-1}; 4) line diagram corresponding to pyrograms 1–3.

cellulose acetate, polyethylene, polypropylene, polyacrylonitrile, natural and synthetic rubbers, barbiturates, phenothiazines, amino-acids, various aromatic compounds, etc.

Let us consider the main fields of application of pyrolytic gas chromatography.

Identification of polymers. A large number of studies have shown that on pyrolysis under standard conditions various polymers give characteristic chromatographic spectra (pyrograms) of the pyrolysis products. An example is provided by the work of Groten[34], who found that almost all specimens of more than 150 different polymers tested gave different pyrograms. Distinct characteristic pyrograms were obtained for polymers with general formula $(CH_2-CHX)_n$, namely polystyrene, poly(vinyl acetate), polypropylene, and poly(vinyl chloride). Marked differences were observed in the pyrograms of cellulose esters (acetate, propionate, and butyrate), natural materials (silk, cotton, and wool), and the polyalkenes with similar structures: polyethylene, polypropylene, poly(3-methylbut-1-ene), and poly-(4-methylpent-1-ene)[34].

The pyrolytic spectra of a large number of plastics have been studied[50]. The specimens studied (0.2–0.5 mg) were subjected to pyrolysis at 650–750°C for 10 s; the pyrolysis products were separated on a column filled with a sorbent consisting of 5% silicone oil on Chromosorb W. It was noted that for polymers with similar structures, differences in the pyrograms are observed only in the peaks corresponding to the "heavy" products.

Janák[24,51] was the first to apply the method involving the identification of substances from the chromatographic spectra of the products of their pyrolysis on a heated spiral to non-volatile organic compounds (barbiturates, amino-acids, and other biochemical materials). Chromatograms for the products of the decomposition of the potassium salts of various amino-acids are given in Fig. 7. The spectrum of the decomposition products depends to a marked extent on the structure of the amino acids subjected to pyrolysis.

Interesting work on the pyrolytic study of proteins was carried out by Winter and Albro[52]. The observed differences in the pyrograms are related to differences in the structures of the materials taken for pyrolysis. For example, egg and serum albumins are characterised by different pyrograms, since the latter contains four times more cystine.

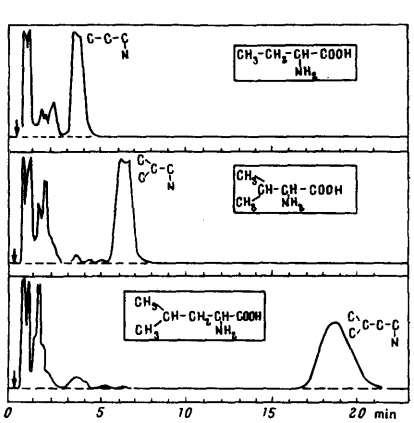


Fig. 7. Pyrograms for various amino-acids (stationary phase squalane, temperature of separation 30°C).

Pyrolytic methods were subsequently developed for the identification of non-volatile aromatic compounds[28,53], benzene clathrates[54], phosphates[55], and other compounds. The results obtained indicate that it is possible to identify polymers and non-volatile compounds from the chromatographic spectra of the products of their degradation under controlled pyrolysis conditions.

The pyrograms obtained in pyrolytic gas chromatography are sometimes figuratively described as "fingerprints", emphasising the empirical nature of the method. For the identification of a polymer, it is necessary to compare its pyrograms with the pyrograms of known specimens and to identify the spectrum. The interpretation of an analysed sample is possible only if the pyrogram of this material has been previously recorded. Inert fillers do not influence the pyrogram of a polymer[26].

In certain instances, definite conclusions regarding the nature and structure of a polymer can be reached merely on the basis of the volatile products obtained. For example, identification of the acid in the products of the pyrolysis of cellulose esters established the nature of the ester being studied.

The characteristic features of the structure of condensation polymers taken for pyrolysis can also be established from the composition of the pyrolysis products, particularly if the polymer contains phenyl groups. The influence of the structure of phenol-formaldehyde resin on its pyrolysis products[56,57] is shown in Fig. 8. It has been shown possible to identify phenolic resins with similar compositions but different degrees of curing[58]. It is pointed out that this identification is impossible by infrared spectroscopy. The analysis of natural and synthetic fibres has been described in detail[59–61].

The extensive application of pyrolytic gas chromatography is being held back, in our opinion, by the lack of standard pyrolysis cells and recommendations on standard conditions of testing.

Analysis of copolymers. In the study of copolymers, it is necessary to have the following information: (1) the concentration of original monomer units in the copolymer, and (2) the structure of the polymeric macromolecule.

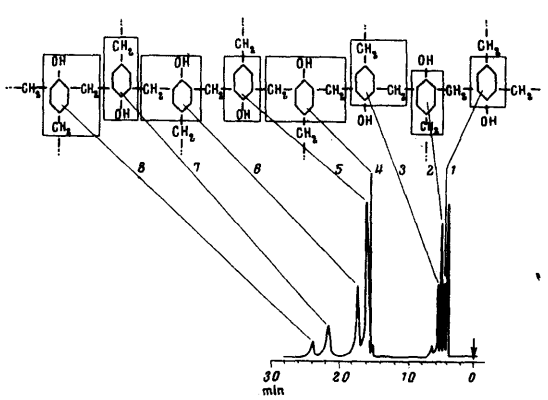


Fig. 8. Correlation between the pyrolysis products and the structure of the original phenol–formaldehyde resin. Temperature of pyrolysis 900°C; capillary column [length 100 m (100 cm? Ed. of Translation), diameter 1 mm]; temperature of separation 170°C; stationary phase polypropylene glycol.
1)–8): identified pyrolysis products.

With certain limitations, pyrolytic gas chromatography can provide this information.

The development of a method for determining the composition of a copolymer usually involves the following operations: (1) the recording of characteristic pyrograms for copolymer specimens with different compositions; (2) the selection of characteristic peaks on the pyrogram, whose magnitudes depend on the composition of the copolymer; and (3) the construction of a calibration curve from the data obtained.

Various copolymers whose compositions have been determined by pyrolytic gas chromatography[57] are listed in the Table, together with the methods of calculation.

An interesting feature is that the results of the determination of the compositions of block copolymers of ethylene and propylene show satisfactory agreement with the results obtained by infrared spectroscopy, and make it possible to determine the composition of the copolymer with an absolute error of 1–3%.[43]

For styrene copolymers it is convenient to select as characteristic peak the peak due to the monomer, the quantity of which (relative to the concentration of styrene in the copolymer) is almost independent of the temperature and of the composition of the copolymer over the range 545–640°C.[71]

The pyrolytic method has been used successfully for the analysis of graft copolymers. The error in composition in the analysis of graft copolymers does not exceed 5 rel.%.[72,73]

The method of pyrolytic gas chromatography is applicable to the analysis of the composition of copolymers even when the use of the classical methods of elementary analysis are restricted by the similarity in the elementary composition of the original monomers.

Esposito[74] proposed the use of the internal standard method in pyrolytic gas chromatography. A solution of the polymer taken as internal standard is suspended with a known quantity of the sample being studied and diluted with a solvent. The resulting solution of the polymers is deposited on a spiral and the pyrolysis is carried out in the usual way (the volatile products are separated by gas chromatography). The concentration of polymer (P) is determined from the formula $P = AB/C$, where A is the corrected area of the characteristic peak, C the area of the peak due to the substance formed by pyrolysis of the internal standard, and B the concentration of internal standard. Esposito[74] used ethyl methacrylate as internal standard. This internal standard method, however, is applicable only to soluble polymers.

It should be emphasised that the method of pyrolytic gas chromatography is sensitive not only to the composition of the copolymer, but also to its structure. This is understandable, since the rupture of chemical bonds in pyrolysis, generally speaking, is not restricted to the boundaries of the original monomeric units. Thus the pyrograms for copolymers with monomeric units alternating in disordered fashion (random copolymers) are in general not identical to the pyrograms of mechanical mixtures of the pure homopolymers, whereas the pyrograms for graft copolymers often correspond to the pyrograms for artificial mixtures of homopolymers with the same composition[72,73]. This result is not unexpected, since if the number of points in the chain of the original polymer at which grafting has taken place is small compared with the number of units in the main chain, the process can be regarded as the degradation of the homopolymers. Two different calibration curves obtained for random copolymers of methyl methacrylate and ethylene and for mechanical mixtures of the corresponding homopolymers[75] are given in Fig. 9. The point corresponding to the graft copolymer lies on the curve for the mechanical mixtures.

Pyrolytic gas chromatography is sensitive to such structural characteristics of the polymer chain as the relative arrangement of the substituents. Groten[34] obtained different pyrograms for polypropylenes with different stereoregularity—atactic and isotactic; this emphasises the extensive possibilities provided by the method.

It has been shown possible[76], in the case of double copolymers of α-alkenes, to use pyrolytic hydrogenation to determine the composition of a copolymer, and also the order of arrangement of the monomer units and the nature of their attachment ("head to head" and "head to tail").

TABLE. Copolymers whose compositions have been determined from pyrograms.

Copolymer	Method of calculation	References
Methyl methacrylate–methyl acrylate	RFA*	62
Methyl methacrylate–ethyl acrylate	RPH**	63
Methyl methacrylate–ethyl methacrylate	RPA	62
Methyl methacrylate (MMA)–ethylene dimethacrylate	AP***(MMA)	62
Methyl methacrylate (MMA)–styrene	HP****(MMA)	64
Butyl methacrylate (BMA)–hexyl methacrylate	AP(BMA)	65
Vinyl chloride (VCl)–vinyl acetate (VAc)	HP(HCl or HAc)	64
Vinyl acetate (VAc)–copolymer	AP (HAc)	66
SBR–polybutadiene	RPH	34
Ethylene–vinyl acetate (VAc)	AP (HAc)	67
Ethylene (ET)–ethyl acrylate	AP (ET)	67
Ethylene–propene, block and random copolymers	RPA	43, 34
Ethylene–butene	RFA	68
Ethylene–methyl acrylate, block and random copolymers	RPA	69
Ethylene–methyl methacrylate, block and random copolymers	RFA	69
Ethylene oxide–propene oxide	RPA	8
Cellulose esters	RPH	34
Plasticisers (PI) in a polymer	HP (PL)	70
Hydroxyethyl group in hydroxyethyl–starch	HP (HCHO)	22

* RPA ratio of peak areas.

** RPH ratio of peak heights.

*** AP area of the peak due to the component indicated in parentheses.

**** HP height of the peak due to the component indicated in parentheses.

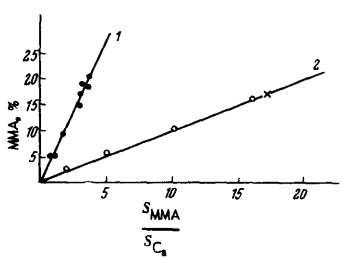


Fig. 9. Dependence of the relative area of two characteristic peaks on the pyrograms of random copolymers (1) and mixtures of polymethyl methacrylate and polyethylene homopolymers (2) on the methyl methacrylate concentration. The point × corresponds to the graft copolymer.

The yield of monomers in the pyrolysis of copolymers which decompose chiefly to the monomer depends on the distribution of the monomer molecules in the copolymer. This is due to the fact that if a polymer decomposes by a radical mechanism with removal of monomer units from the ends of the polymer molecules, the probability of removal of the next monomer unit depends on its immediate neighbour. A method has been developed for calculating the structures of copolymers from the quantity of monomers formed on pyrolysis[77]. The corresponding probabilities can be determined by pyrolysis of copolymers with known composition. The method was tested using styrene–acrylonitrile and styrene–methyl methacrylate copolymers.

In all the above applications of the method, the determination of the individual compositions of the products is not necessary. The study of the mechanism of degradation is a much more complex problem, since it is necessary to obtain as far as possible the complete spectrum of pyrolysis products and to determine their qualitative composition. In these instances it is desirable to carry out the pyrolysis in thin films, to use capillary columns with temperature programming[48], and to use specific, for example chemical, methods of peak identification[78]. Chromatography combined with mass spectroscopy will obviously be of considerable assistance in the interpretation of the chromatographic peaks.

Berton[79], for the example of a number of polymeric materials, proposed the use of selective galvanic detection of the pyrolysis products, based on the reaction of the pyrolysis products with the electrolyte of the detector. This reaction leads to a change in the polarisation of the electrode and the electric current. The nature of the electrolyte determines the classes of compounds detected. The use of a saturated solution of chromium(VI) oxide in nitric acid as electrolyte makes it possible to detect alcohols, aldehydes, and various unsaturated substances, with a high sensitivity[79]. The use of galvanic detection with the above electrolyte appears particularly promising for the analysis of the products of oxidative pyrolysis.

In some instances the identification of pyrolysis products can be carried out gas-chromatographically from their molecular weights, using a density detector and carrier gases with different molecular weights[80] or two katharometers, one of which operates as a density detector[81]. In the latter instance, when certain conditions are satisfied, the ratio of the signals from these detectors is directly proportional to the molecular weight of the substance. The study of processes which take place in polymers at elevated temperatures and are accompanied by the liberation of products volatile at the temperature of the experiment is also of interest.

Garzó and Székely[82] studied the thermal processes involved in the curing, decomposition, and depolymerisation of silicone polymers, by using a carrier gas to carry the volatile reaction products, at measured time intervals, from the micro-reactor into the chromatograph.

Finally, it may be noted that the published experimental material makes it possible to recommend the pyrolytic method for research purposes, and in some instances for technological control. A necessary condition for the extensive introduction of this method, however, is the development of standard apparatus and standardisation of the pyrolysis conditions (the size of sample, temperature of pyrolysis, conditions of chromatographic separation, etc.).

Future Prospects for the Development of Degradative Chromatographic Methods

In the study of the composition and structure of polymers, it is undoubtedly desirable, in addition to pyrolysis, to apply to polymers other, possibly more structurally sensitive, degradation methods, and also various combinations of these methods. Thus pyrolytic gas chromatography can be regarded as one version of degradative gas chromatography.

Scholz and coworkers[83] proposed the characterisation of polymers from the spectra of the products of their oxidative degradation. The polymer being studied is deposited on a solid inert carrier and placed in a short additional column placed between the device used to introduce the sample and the chromatographic separating column. The temperature of the additional steel column containing the polymer being studied can be controlled by means of a thermostat in the range 100–600°C. Oxidation of the polymer takes place on contact with oxygen (1 cm^3 of oxygen is introduced into the stream of inert carrier gas). The volatile oxidation products are carried by the stream of carrier gas into the chromatographic column for separation. The spectrum of volatile products from the oxidative degradation is characteristic for each polymer.

As noted above, a combination of thermal degradation and thermal oxidation has been used to identify pyrolysis products and to study the mechanism of pyrolysis[49]. It has been proposed[84] that the degradation of the polymer be carried out in a current of carrier gas under the conditions of the electric discharge (300 V, 1 mA). It has been shown for several polymers that the composition of the degradation products corresponds to the products formed under the conditions of pyrolysis at 600°C.

Kolbanovskii and coworkers[85], in the Institute of Petrochemical Synthesis, developed a new method of degradative gas chromatography—radiochemical chromatography.

In radiochemical chromatography, the polymer is characterised by the spectrum of volatile radiolysis products. After γ-irradiation (dose ~ 100 Mrad) of a specimen of the polymer at room temperature in an evacuated glass ampoule, the gaseous radiolysis products were analysed. About 50 specimens of different polymers were studied, and a characteristic spectrum of radiolysis products was obtained for each polymer. The method is sensitive to the structure of the polymer and the composition of the copolymer. Different line diagrams were obtained for natural rubber, gutta percha, SKD synthetic rubber, and *trans*-polybutadiene. All four specimens, which taken in pairs differ only in their spatial configuration, gave different spectra. In a study of the radiolysis of copolymers, a linear relationship was observed between the relative yield of ethylene and the concentration of acrylonitrile in its copolymer with butadiene. The method is very sensitive to branching of the carbon chain. High-pressure and low-pressure polyethylenes also give different spectra of products from radiochemical degradation.

In addition to purely analytical applications, the use of degradation methods to study the thermal stability of polymers and non-volatile compounds in various gaseous media (and also under the influence of radiation), for the rapid determination of the efficiency of various inhibitors, etc., is of particular interest. The possibility of carrying out the studies with very small quantities of substance, the simplicity of the method, and its high resolving power are opening up extensive possibilities for the application of gas chromatography for the estimation and study of non-volatile polymeric materials.

The development of new versions of degradative gas-chromatographic methods will undoubtedly open up new horizons in the study of polymeric materials.

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THE CYCLOPROPENYL CATION

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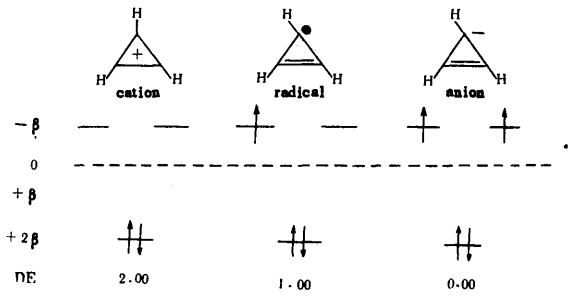
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1. THE CYCLOPROPENYL CATION

A considerable amount of work has now been published on the three-membered analogue of the tropylium cation—the aromatic cyclopropenyl cation—and the present paper gives a brief survey of the literature on the preparation and the electrophilic character of this cation. A recent review[1] of the reactions of the cyclopropenyl cation and allied compounds paid very little attention to this question.

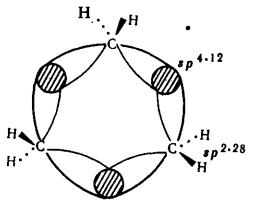
According to Hückel's rule, a planar monocyclic system having trigonal hybridisation of the carbon atoms and containing $4n + 2$ π-electrons possesses a filled electronic configuration and enhanced stability[2]. The simplest system satisfying Hückel's aromaticity conditions with $n = 0$ is the cyclopropenyl cation.



The accompanying diagram shows the molecular levels and the delocalisation energies (DE) for the cyclopropenyl cation, radical, and anion calculated by the LCAO-MO method[3]. The above scheme shows that the cation possesses the maximum delocalisation energy, while the anion has DE = 0 and is in a triplet state. Consequently these species can be arranged in the sequence—cation > radical > anion—of diminishing stability. For the cyclopropenyl cation DE = 2β, which is somewhat lower than the delocalisation energy of the tropylium cation (2.99β),[3] but considerably exceeds that for the allyl cation (0.8β).[4] Nevertheless, in spite of the considerable delocalisation energy, the cyclopropenyl cation itself has not yet been obtained, and several authors[1] cast doubt on the possibility of its existence. The strongest destabilising influence on the cation is exerted by the angular strain of the three-carbon ring. It is usually considered that the energy of the angular strain in cyclopropane is 27.6 kcal mole^{-1},[5] and for cyclopropene an estimate of 55 kcal mole^{-1} has been made[6]. This energy would increase still more in the cation, probably to 74 kcal mole^{-1} [1,7] as a consequence of the change in the valency state of the carbon atoms on formation of the cation from cyclopropene.

Baeyer's theory of angular strain has been discussed by Walsh[8] and also by Coulson and Moffit[9]. They reached

the conclusion that a satisfactory description of the state of the bonds in cyclopropane can be obtained only on the assumption that the type of hybridisation of the atomic orbitals of the ring carbon atoms is other than sp^3:



Coulson and Moffit calculated that the atomic orbitals involved in the formation of C–H bonds have $sp^{2.28}$ hybridisation.

It must be noted here that, in calculating the energies of strain in cyclopropane and cyclopropene from their heats of combustion or heats of hydrogenation compared with those of unstrained cycloalkanes, these workers took no account of the change in valency state of the carbon atoms on passing from unstrained to strained rings. Actually, however, such transfer of a carbon atom is accompanied by a change in its valency state from the first to the second in cyclopropane, and to the second and the third in cyclopropene. We have attempted to allow for these changes [10] by using in the calculation values of the C–H bond energies in ethylene and acetylene [11], and have thus obtained higher values for the energies of strain in cyclopropane and cyclopropene than had been accepted hitherto (48.6 and 87 compared with 27.6 and 55 kcal mole^{-1} respectively). It is quite obvious that the energy of strain for the cyclopropenyl cation, too, will be greater than the value calculated previously (102.5 instead of 74 kcal). Results obtained by Wiberg et al. on the heats of dissociation of propene and cyclopropene into a hydride ion and the corresponding carbonium ions are consistent with these calculations. They show [6] that the cyclopropenyl cation is only 10 kcal more stable than the allyl cation. Such a small difference can be explained by the presence of a high energy of strain in the cyclopropenyl cation, which brings its delocalisation energy close to that for the allyl cation.

Another cause of the instability of the cyclopropenyl cation may be electrostatic repulsion between positively charged carbon atoms of the three-membered ring. It must be regarded as proved that, in this cation just as in the tropylium cation, the positive charge is uniformly distributed among all the ring carbon atoms. X-Ray examination of triphenylcyclopropenyl perchlorate [12] has shown that the interatomic distances in the C–C bonds of the three-membered ring all have the same value of 1.37 Å. Hence it follows that the charge in this compound is uniformly distributed among the three carbon atoms forming the ring.

2. CYCLOPROPENYL CATIONS CONTAINING ARYL AND ALKYL SUBSTITUENTS

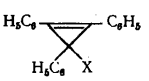
Manatt and Roberts [13] calculated the delocalisation energies of the mono-, di-, and tri-phenylcyclopropenyl cations by the simple Hückel molecular-orbital method. Table 1 gives the values calculated by these [13] and other authors [3,7,14,15] for the total and excess delocalisation energies of these cations. The latter parameter represents the difference between the total delocalisation energy of a given cation DE and the delocalisation energy of the cyclopropenyl cation itself ($DE_0 = 2.00$) together with the sum of the delocalisation energies of the phenyl groups (ΣDE_{ph}): $\Delta DE = DE - DE_0 - \Sigma DE_{ph}$.

TABLE 1. Total and excess delocalisation energies (in β-units) of phenylated cyclopropenyl cations.

No. of C_6H_5	DE	ΔDE	Ref.
0	2.00	—	3
1	4.39	0.39	13
	4.40	0.40	14
2	6.70	0.70	13
	6.78	0.78	7,14
3	9.19	1.19	13
	9.16	1.16	15

Table 1 shows that replacing a hydrogen atom in the cyclopropenyl cation by a phenyl radical increases both the total and the excess delocalisation energy of the ion. Breslow and his coworkers studied the influence of the number and nature of substituents on the ease of formation of cyclopropenyl cations [7,16,17], and found that their stability increases primarily with increasing degree of substitution. From this it followed that the cyclopropenyl cation itself will be the most unstable. It was further found that, with the same degree of substitution of the ring, electron-donor substituents have a more favourable effect than have electron-acceptor substituents on the formation of the cation. Dialkoxycyclopropenyl cations proved to be more stable than diaryloxycyclopropenyl cations [18–20].

The ease of formation of a cyclopropenyl cation from a cyclopropene derivative depends both on the ring substituents and on the nature of the anion which is eliminated. Thus in triphenylcyclopropenyl bromide, for example, the bromine is present as an anion, whereas in tetrabromocyclopropene all the bromine atoms are combined covalently [21]. A series of cyclopropene derivatives is now known in which a definite relationship can be observed between the nature of the atom of group X and the character of the C–X bond in compounds of the type



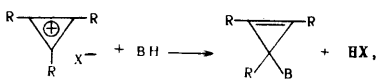
where X = H, OCH_3, CN, 2,4,5-$(NO_2)_3C_6H_2O^-$, Br^-, BF_4^-. In the first three of these compounds the C–X bond is found to be covalent, and in the latter three it was ionic. A similar series is known also for derivatives of the tropylium cation [22]. Vol'pin et al. [23] showed that the weakest acid whose anion forms an ionic compound with the tropylium cation is isocyanic acid HNCO ($K_a = 1.2 \times 10^{-4}$), while the strongest acid with which the same cation will give a covalent compound is benzoic acid ($K_a = 6.3 \times 10^{-5}$).

3. REACTIONS OF CYCLOPROPENYL CATIONS WITH WATER, ALCOHOLS, AND OTHER NUCLEOPHILIC REAGENTS

As follows from the preceding Section, a greater or smaller concentration of cationic charge on the carbon atoms of the three-membered ring is determined by the number and nature of the substituent groups. The more delocalised is the cationic charge on the substituent groups,

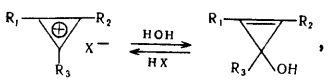
the greater its stability and the smaller the electrophilic activity. With less delocalisation of the charge, the electrophilic properties of the cation will be more strongly developed.

Just like the aromatic tropylium cation, the cyclopropenyl cation can take part in electrophilic substitution reactions, represented by the general equation



where R = Alk, Ar, or Hal; BH is a nucleophilic reagent, e.g. HOH, CH_3OH; and X = Br, BF_4, ClO_4.

The simplest reaction of this type is the hydrolysis of cyclopropenyl salts to the corresponding cyclopropenols. In this case the electrophilic cation attacks the nucleophilic water molecule. Breslow et al. have shown[7] that this can be regarded as an equilibrium:



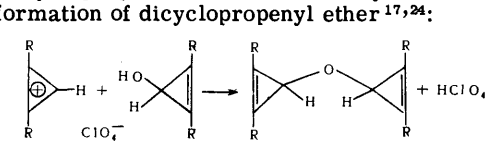
where HX is the conjugate acid. The equilibrium constant K_{R^+} is given by the equation

$$K_{R^+} = \frac{[C_3H_3OH]\cdot[H^+]}{[C_3H_3^+]}$$

where $[C_3H_3OH]$ and $[C_3H_3^+]$ are the concentrations of cyclopropenol and cyclopropenyl cation respectively. This constant can be more conveniently expressed in the form $pK_{R^+} = -\lg K_{R^+}$, which is numerically equal to the pH at which the cyclopropenyl salt is 50% converted into the cyclopropenol.

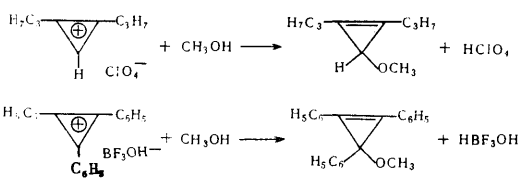
Table 2 lists experimental values of pK_{R^+} obtained by Breslow and his collaborators, and of ΔDE for the cyclopropenyl cations calculated by the LCAO-MO method. The latter represent the difference in delocalisation energy between the cation and the corresponding cyclopropenol. Table 2 clearly shows that ΔDE and pK_{R^+} are directly related. It is noteworthy also that, while the triphenylcyclopropenyl cation is stable at pH 3, the tripropylcyclopropenyl cation is stable even at pH 7. Hence it may be concluded that alkyl groups stabilise the cyclopropenyl cation better than do aromatic groups.

In the case of the above equilibrium hydrolysis of disubstituted cyclopropenyl salts, account must be taken of the possibility that the cation will undergo another, irreversible reaction, involving its hydrolysis product, dipropyl(or diphenyl)cyclopropenol. This secondary reaction results in the formation of dicyclopropenyl ether[17,24]:

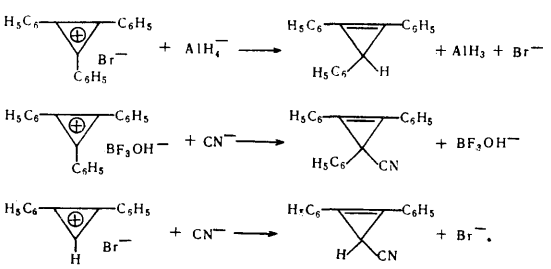


where R = C_3H_7, C_6H_5. Since the rate of the equilibrium reaction far exceeds that of the secondary reaction, the occurrence of the latter does not complicate study of the former: equilibrium is established before appreciable quantities of the dicyclopropenyl ether are able to accumulate in the reaction products.

Substitutions in which the cyclopropenyl cation acts as an electrophilic reagent take place also with alcohols. For example, dipropyl- and triphenyl-cyclopropenyl cations react with methanol to form respectively methoxydipropylcyclopropene[17] and methoxytriphenylcyclopropene[25]:



Like the tropylium cation the cyclopropenyl cation reacts also with lithium tetrahydroaluminate[26] and with potassium cyanide[16,25,27], the tetrahydroaluminate and cyanide anions acting as nucleophiles. The reaction products are in both cases covalently bound compounds. Examples of these reactions given below involve the tri- and di-phenylcyclopropenyl cations



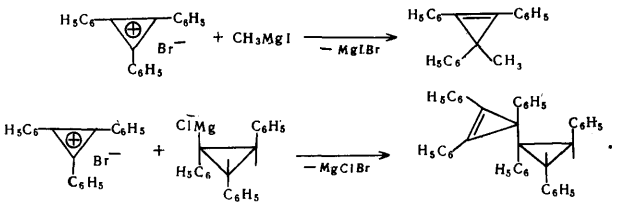
The electrophilic character of the cyclopropenyl ion is exhibited also in its ability to react with other typical nucleophilic reagents, such as organomagnesium and organolithium compounds. The triphenylcyclopropenyl cation reacts with methylmagnesium iodide and with *trans*-1,2,3-triphenylcyclopropylmagnesium chloride, to yield

TABLE 2. Influence of substituents on the position of the cation–cyclopropenol equilibrium.

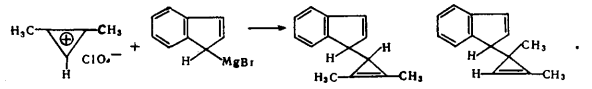
Substituted cyclopropenyl cation	ΔDE[a]	ΔDE[b]	pK_{R^+} ±0.05	Ref.
Unsubstituted	2.00	—	>0[c]	16
			−6.3[c]	17
Dipropyl	—	—	+2.68[d]	17
Tripropyl	—	—	+7.2[d]	17
Diphenyl	1.90	3.00	−0.67[e]	16
			+0.32[f]	16
Propyldiphenyl	—	—	+3.80[e]	17
Triphenyl	2.31	3.46	+3.1[d]	17
			+2.80[e]	7
			+3.18[f]	16
Diphenyl-*p*-methoxyphenyl	2.34	3.53	+4.00[e]	7
Phenyldi-*p*-methoxyphenyl	2.37	3.58	+5.16[d]	17
			+5.22[e]	7
Tri-*p*-methoxyphenyl	2.40	3.64	+6.50[d]	17
			+6.42[e]	7

(*a*) Calculated by the simple Hückel method.
(*b*) Calculated by the ω-technique.
(*c*) Values of pK_{R^+} for the unsubstituted cyclopropenyl cation obtained by extrapolating experimental values of pK_{R^+} for di- and tri-substituted cations.
(*d*) Equilibrium in 50% aqueous acetonitrile.
(*e*) Equilibrium in 23% aqueous alcohol.
(*f*) Equilibrium in water.

respectively methyl-1,2,3-triphenylcyclopropene and 1,2,3-triphenyl-(*trans*-1,2,3-triphenylcyclopropyl)cyclopropene [28]:

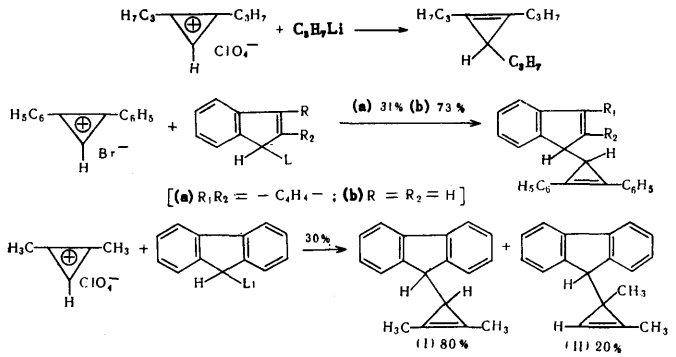


Interaction of the dimethylcyclopropenyl cation with indenylmagnesium bromide gives a mixture of two isomeric indenyldimethylcyclopropenes [28]:



The appearance of two isomers in the reaction product indicates that the positive charge in the cyclopropenylium cation is distributed among its three ring carbon atoms, and is not fixed on one of them. Since two of the three positions of the charge in the ring are equivalent, two—not three—isomers are formed.

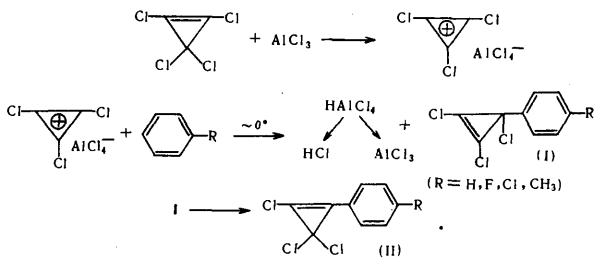
In all the reactions of organolithium compounds with cyclopropenyl cations, the electrophilic cation displaces the metal in the form of a cation from the organolithium compound [17,29,30]:



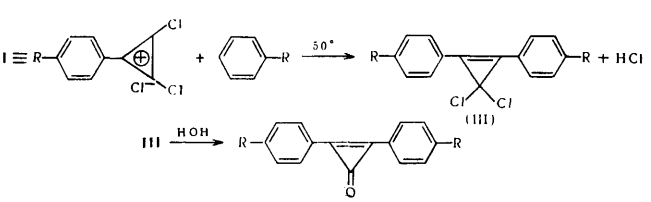
In conformity with the result observed for the reaction of dimethylcyclopropenyl with indenylmagnesium bromide, two isomeric cyclopropene hydrocarbons might have been expected to result also from the interaction of diphenyl- and dimethyl-cyclopropenyl cations with organolithium compounds. This has been confirmed, however, only for the reaction of the dimethylcyclopropenyl cation with fluorenyl-lithium. In other cases the expected isomers could not be isolated. The fourfold yield of the isomer (I) relative to that of (II) is probably to be explained not only by the not entirely uniform distribution of the cationic charge inside the cyclopropenyl ring but also by the unexpected magnitude of the steric hindrance accompanying the attack of the nucleophilic reagent on the electrophilic centres of the cation—ring carbon atoms 1 (or 2) and 3.

4. AROMATIC SUBSTITUTIONS INVOLVING THE CATIONS

The cyclopropenyl cation can take part in the electrophilic substitution of an aromatic nucleus, just like other carbonium ions. An example is the interaction of the trichlorocyclopropenylium cation with benzene, toluene, chlorobenzene, and fluorobenzene, studied by Tobey and West [31,32]. The reaction proceeds under the conditions of the Friedel–Crafts reaction. The aluminium chloride employed as catalyst is necessary to convert the tetrachlorocyclopropene into a trichlorocyclopropenyl salt. If the reaction is conducted at 0°C, it can be represented by the equations



The trichloro-derivative (I), which is the normal product of reaction between the cation and an aromatic hydrocarbon or its halogeno-derivative, cannot be isolated, since under the conditions of the reaction it undergoes allylic rearrangement into the isomer (II), which is more stable as a consequence of conjugation of the endocyclic double bond with the aromatic ring. This isomer is the final product of the Friedel–Crafts reaction. However, the conversion of the cyclopropene (I) into (II) is not a simple allylic isomerisation. It must probably be interpreted as reaction of the aryldichlorocyclopropenyl cation, already present in (I), with its own chloride anion, which attacks the sterically least hindered site in this cation. This is consistent with the fact that, when the reaction with the trichlorocyclopropenyl cation is conducted at a higher temperature (50°C), the reaction products are found to contain diphenyl-*gem*-dichlorocyclopropenes (III), formed by secondary interaction of (I) with the initial aromatic derivative. The compounds (III) are readily converted by water into the corresponding cyclopropenones [31]:

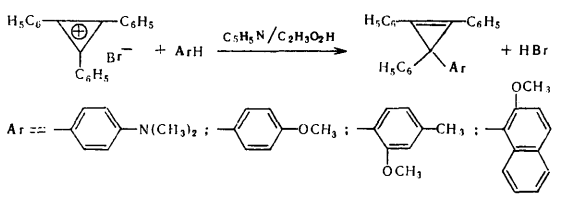


where R = H, F, Cl, CH_3.

This reaction can thus be regarded as a kind of "capture", by the aromatic hydrocarbon or its halogeno-derivative, of the saltlike compound (I), which exists only at a relatively low temperature. Attempts to obtain in this way triarylcyclopropenyl cations or tetra-arylcyclopropenes by the more prolonged and severe heating of trichlorocyclopropenyl tetrachloroaluminate with the same benzene derivatives proved unsuccessful [32].

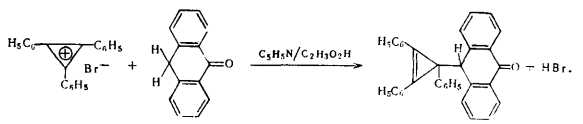
In contrast to tetrachlorocyclopropene, a cyclopropenyl cation is already present in triphenylcyclopropenyl bromide. In this case, therefore, cyclopropenylation of the aromatic ring can be carried out even in the absence of aluminium chloride [33]. No other cycloalkenyl or alkyl

halide alkylates an aromatic ring in the absence of a catalyst. This can be regarded as some indication of a cationic mechanism for the Friedel–Crafts reaction.

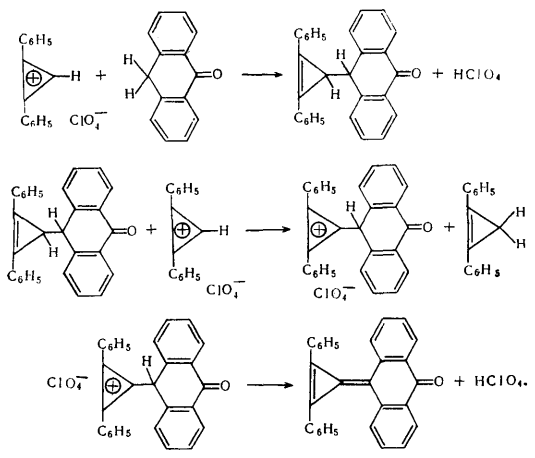


5. REACTIONS OF CYCLOPROPENYL CATIONS WITH COMPOUNDS CONTAINING AN ACTIVE METHYLENE GROUP

The literature contains a large number of examples of the reactions of tropylium cations with compounds containing a reactive methylene group. Little work has been done on such reactions with cyclopropenyl cations. It is known, however, that heating triphenylcyclopropenyl bromide with anthrone in the presence of pyridine and acetic acid yields 10-(1,2,3-triphenylcycloprop-2-enyl)anthrone[33]:

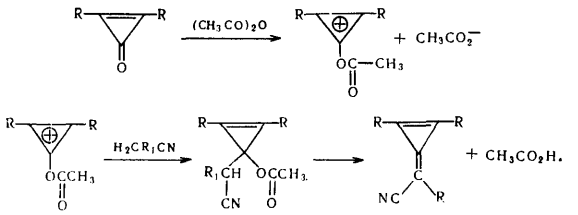


Another example is the reaction between anthrone and diphenylcyclopropenyl perchlorate. This gave a new compound of the triafulvene (methylenecyclopropene) series[33], 10-(2,3-diphenylcycloprop-2-enylidene)anthrone. The formation of this ketone can be represented by the following sequence of reactions



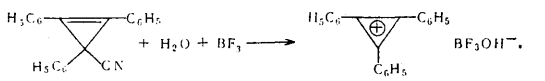
The first stage in the process is electrophilic substitution of a methylene proton in anthrone by the diphenylcyclopropenyl cation with formation of 10-(2,3-diphenylcycloprop-2-enyl)anthrone. In the second stage the cyclopropenyl cation reacts with the reaction product of the first stage, the latter losing a hydride ion and anthronyldiphenylcyclopropenyl perchlorate being formed. In the third (and last) stage of the reaction, perchloric acid is eliminated, and the final product—10-diphenylcyclopropenylideneanthrone—is obtained.

Compounds of the triafulvene series are formed also when dipropyl- and diphenyl-cyclopropenones are heated with malononitrile or cyanoacetic ester in the presence of acetic anhydride[20,34–38]. Available data on the mechanism of this reaction indicate that the primary product is the acetoxydipropyl(or diphenyl)cyclopropenyl cation, formed by the action of acetic anhydride on the dipropyl(or diphenyl)cyclopropenone[37]. The resulting cation then undergoes a substitution reaction with the labile hydrogen atoms of the methylene group in the malononitrile (or cyanoacetic ester). Subsequent elimination of acetic acid from the cyclopropenyl acetate formed as an intermediate stage leads to the triafulvene:

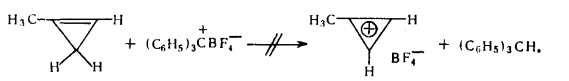


6. METHODS OF PREPARING CYCLOPROPENYL CATIONS

The first experimental confirmation of the existence of the two-π-electron aromatic cyclopropenyl system was obtained by Breslow, who treated cyano-1,2,3-triphenylcyclopropene with a moist ethereal solution of boron trifluoride and isolated triphenylcyclopropenyl hydroxotrifluoroborate[27]:

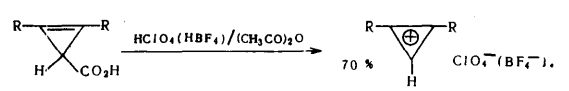


The unsubstituted cyclopropenyl cation has not yet been obtained[6]. Several investigators consider, however, that the ion $C_3H_3^+$ (M = 39), which is frequently met in the mass spectra of various organic compounds, has the cyclopropenyl cation structure rather than that of a prop-2-ynyl or allenyl cation[6,39–41]. Nor has it proved possible to obtain the methylcyclopropenyl cation[42] by abstracting a hydride ion from the hydrocarbon by means of the triphenylmethyl cation:

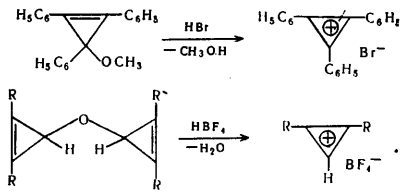


Formation of certain mono- and di-substituted cyclopropenyl cations has been observed mass-spectrometrically in the fragmentation of monocyclic 2-pyrones[43].

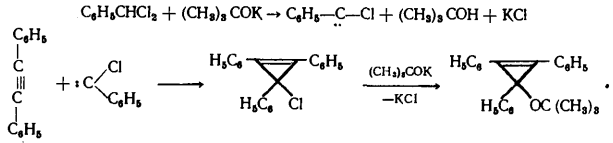
The simplest stable cation known at the present time is the dimethylcyclopropenyl ion[28]. To obtain this ion, and also several of its disubstituted homologues, wide use is made of a method proposed for preparing the tropylium cation from cycloheptatrienecarboxylic acid[44]. This method consists essentially in converting the cyclopropene(or cycloheptatriene)carboxylic acid, by means of a solution of perchloric or fluoroboric acid in acetic anhydride, into the cyclopropenyl (or tropylium) perchlorate or fluoroborate[17,26,28,45]:



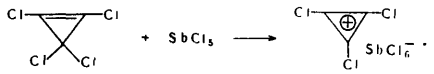
Good yields of cyclopropenyl cations are obtained also by the cleavage of cyclopropenyl ethers [7,16,17,19,25,46] with mineral acids:



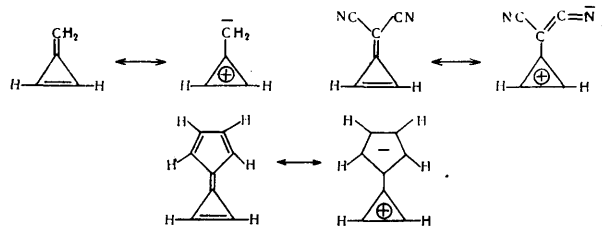
Ethers of cyclopropenols can be obtained by the interaction of arylchlorocarbenes with mono- or di-arylacetylenes in the presence of excess of an alkali-metal alkoxide: e.g.



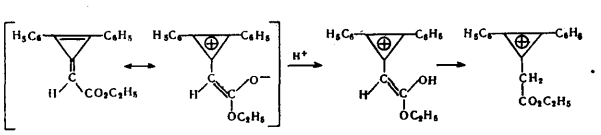
As already mentioned above, tetrachloro- and tetrabromo-cyclopropenes react with Lewis acids ($AlCl_3$, $SbCl_5$) to give stable trihalogenocyclopropenyl cations [21]:



Vigorous attempts have recently been made to synthesise methylenecyclopropene (triafulvene) and its derivatives [47-49]. Success has been achieved with derivatives containing electronegative substituents (CN, $COOC_2H_5$) in the methylene group of triafulvene [34-36,38,50,51] and with compounds having this group in a pentadiene ring (calicenes) [20,28-30,37,52,53]. Calculations made by the simple Hückel method indicate that triafulvene should be relatively stable (DE = 0.96β [3,13]). This result and also the calculated dipole moment of triafulvene (μ = 5.26 [2], 5.00 [54], 1.21 [55] D) are consistent with the view [34] that a considerable contribution to its ground state is made by a dipolar structure.



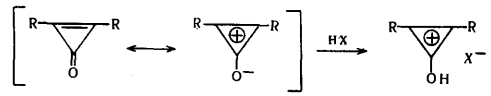
This contribution can be strengthened by introducing electronegative substituents into the methylene group of the triafulvene. The presence of a dipolar structure in the ground state of the molecule is indicated by the tendency of certain triafulvene derivatives to form salts of the corresponding cyclopropenyl derivatives by the action of strong mineral acids: e.g. [51]



This reaction has quite often been used to confirm the structure of triafulvenes [20,28,46,50].

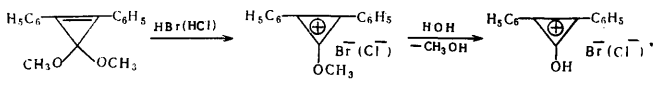
Quantum-mechanical calculation by the LCAO-MO method indicates [3] that cyclopropenylidenecyclopentadiene (calicene) should possess a delocalisation energy of 2.94β (almost 50% greater than that of benzene) and exhibit a dipole moment, as a consequence of its tendency to form a dipolar structure [53] in which the three-carbon ring is positively charged, while the five-carbon ring is negatively charged.

The oxygen analogue of methylenecyclopropene—cyclopropenone—is unknown, like methylenecyclopropene itself. However, several disubstituted cyclopropenones are now known [18,19,56-60]. In agreement with theoretical predictions, the physical and chemical properties of these compounds indicate a considerable contribution by a dipolar structure to the ground state. As a result, cyclopropenones are able to yield salts with strong mineral acids:

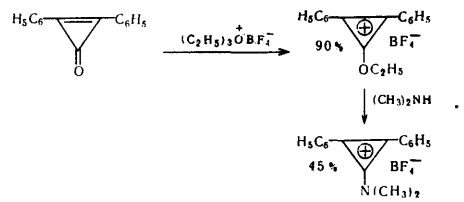


where R = C_3H_7, C_6H_5 and X = Cl, Br.

This reaction involves the formation of hydroxycyclopropenyl cations. The hydroxydiphenylcyclopropenyl cation can be obtained also by dealkylating 3,4-dimethoxydiphenylcyclopropene with a hydrohalic acid [56], and then hydrolysing [19,57,58] the methoxydiphenylcyclopropenyl cation formed as intermediate:

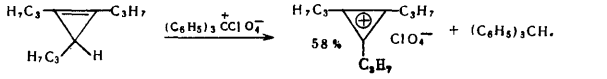


Several new derivatives of the cyclopropenyl cation have recently been prepared from diphenylcyclopropenone [19]:



On treatment with triethyloxonium fluoroborate, diphenylcyclopropenone is converted into ethoxydiphenylcyclopropenyl fluoroborate, which with dimethylamine yields *NN*-dimethylaminodiphenylcyclopropenylium fluoroborate. This last compound is so difficult to hydrolyse with water that it can be recrystallised from it.

At the present time the most widely used method for obtaining cyclopropenyl cations is abstraction of a hydride ion from derivatives of cyclopropene [17,28-30,61,62]: e.g.



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"LADDER" AND "PARQUET" POLYMERS

Yu. E. Doroshenko

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INTRODUCTION

The accompanying diagram illustrates schematically the molecular structures of all polymers known at the present time.

Polymers of types *1*, *3*, and *6* have been studied for many years. Research workers have recently been paying increasing attention to polymers whose molecules correspond to the remaining three types (*2*, *4*, *5*). This is not accidental, since regularly arranged cyclic units confer on the polymer exceptionally high resistance to the action of temperature, radiation, and corrosive media. This applies especially to aromatic systems.

Structures of types *4* and *5* are distinguished from the others by the presence of regularly fused cyclic systems. The structure of these cyclic systems resembles either a rope ladder, whence the name "ladder polymers", or a parquet, when an ideal network structure is formed ("parquet polymers"). These two types of macromolecular structures will be briefly discussed in the present review.

I. LADDER POLYMERS

The rings in ladder polymers comprise either carbon atoms alone (carbocyclic ladder polymers), carbon together with various heteroatoms, such as oxygen, nitrogen, phosphorus, etc. (heterocyclic ladder polymers), or no carbon at all. The last type include inorganic and organoelementary polymers, the rings of which contain oxygen atoms alternating with silicon, titanium, etc. atoms to which are attached organic or inorganic substituents.

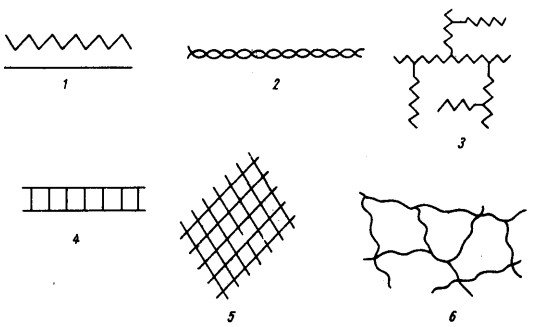


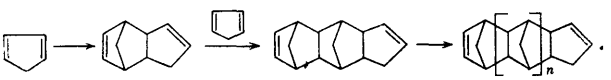
Diagram of structure of various polymers:
1) linear polymers; 2) spiran polymer; 3) branched polymer; 4) ladder polymer; 5) parquet polymer; 6) three-dimensional network polymer.

A. CARBOCYCLIC LADDER POLYMERS

This fairly considerable group of ladder polymers may contain rings of two types—(1) alicyclic or hydroaromatic and (2) aromatic—which show fundamental differences in modes of preparation and in properties, so that the two groups will be considered separately.

1. Alicyclic Ladder Polymers

A representative of ladder polymers having five-membered carbon rings, which has been known for a long time, is polycyclopentadiene. At room temperature cyclopentadiene readily forms a dimer, and by prolonged heating Staudinger[1] was able to obtain tri-, tetra-, and pentacyclopentadienes and products of higher molecular weight. Polymerisation proceeds by the Diels–Alder reaction[2–4] as follows:



The melting point increases sharply with increase in molecular weight. Thus the di-, tri-, tetra-, and pentamers have melting points of 32°, 60°, 190°, and 270°C respectively, while polymers of higher molecular weight soften with decomposition at 373°C. Tetracyclopentadiene is readily soluble in benzene, whereas pentacyclopentadiene is very sparingly soluble, and the products of higher molecular weight are completely insoluble in benzene[1].

Cyclic polymers of butadiene, isoprene, and their derivatives are of great theoretical and practical interest. A good review of cyclised rubber has been given by van Veersen[5,6] who has made a valuable contribution to the study of the structure, properties, and methods of preparation of this polymer.

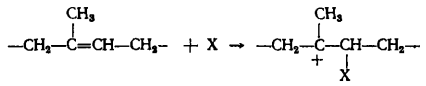
Harries[7] first reported that he had obtained an insoluble cyclisation product of natural rubber by treating a benzene solution of the latter with sulphuric acid. Later Kirchhof[8] and Staudinger[9] observed that the physical and chemical properties of rubber were greatly changed by the action of sulphuric acid. Staudinger[9] obtained a brittle solid having the same empirical formula as the original rubber. Fisher[10] developed the technical production of cyclised rubber: a mixture of rubber, sulphuric acid, and kieselguhr (or titanium oxide) was heated and stirred at 130°C. Besides sulphuric acid, aromatic sulphonic acids could be used successfully.

Bruson et al.[11] cyclised rubber in solution, using such Friedel–Crafts catalysts as $SnCl_4$, $TiCl_4$, and $FeCl_3$ for this purpose.

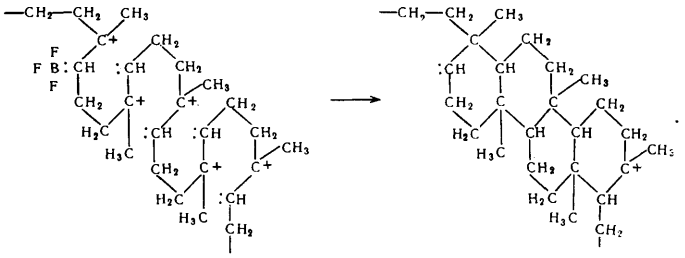
Cyclisation was found to take place under the influence of electrophilic reagents[12] or on heating[13]. Staudinger showed[14] that cyclised rubber can be obtained from hydrochlorinated rubber by the prolonged heating of a solution of

the latter in toluene in the presence of zinc chloride. Hydrobrominated or hydriodinated rubber can also be used for this purpose.

A mechanism of chain initiation and growth in the cyclisation of rubber was suggested by van Veersen[5], according to which a double bond first interacts with an electron acceptor X;



where X = H^+, $AlCl_3$, BF_3. The resulting carbonium ion, in its turn, reacts as an acceptor for the next double bond:



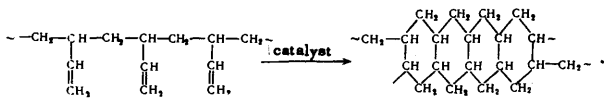
In this way macromolecules containing fused six-membered rings are formed. In van Veersen's view[5] the probability of interaction between different macromolecules is very small, and cyclised rubber represents an aggregate of fused six-membered rings separated by shorter or longer polyisoprene sections.

With increasing degree of cyclisation the material becomes harder and harder, and when the content of cyclic groups is sufficiently large, brittleness ensues. Polymers in which 60–80% of the double bonds have disappeared by cyclisation have softening points of 50–80°C.[6] The cyclised polymer is stable to the action of 10% H_2SO_4 and 50% NaOH at room temperature, but it is rapidly oxidised by oxygen owing to the presence of a tertiary hydrogen atom.

Considerable progress has been made during recent years in the synthesis of polymers using catalysts of ionic type. Attention has been paid also to diene monomers. It was found that the chemical nature, composition, and quantity of the ionic catalyst has a fundamental effect on the structure, properties, and yield of polymers obtained from conjugated dienes. It was established that insoluble products can be formed by the polymerisation of dienes in the presence of titanium tetrachloride and organometallic compounds[15–19].

When isoprene is polymerised in the presence of triethylaluminium and titanium tetrachloride with the molar ratio of the components of the catalyst below 0.8 (especially at 0.3), a large amount of gel is formed[17]. A similar effect has been observed in the case of the triisobutylaluminium–titanium tetrachloride catalytic system[17,18]. When the molar ratio of these components is 1.25 or less, the polymerisation of butadiene in a solvent also results in products which are insoluble in hot xylene[19].

Kropacheva et al.[16] obtained two types of polymers—an elastomer soluble in petroleum ether and an insoluble amorphous powder—in an investigation of the polymerisation of isoprene in petroleum ether solution at room temperature in the presence of equimolecular proportions of isopentylsodium and titanium tetrachloride. Analogous products are formed in the polymerisation of butadiene. The yield of the insoluble solid polymer increases with increase in the quantity of titanium tetrachloride, and it is the sole product when the ratio of isopentylsodium to titanium tetrachloride is 1 : 3. Solid polybutadiene softens and begins to decompose at about 400°C. Such a high softening point is due to the cyclic structure of the polymer, which is formed according to the scheme



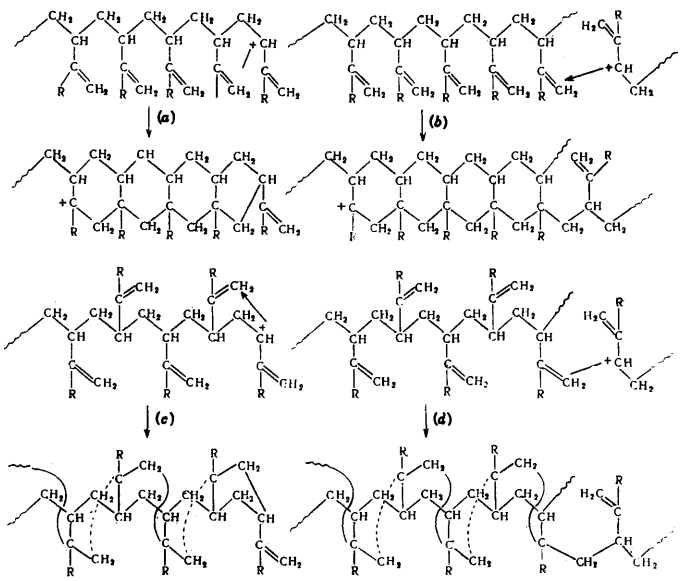
In an investigation of the isomerisation of natural rubber, Dolgoplosk and his collaborators have shown[15,16,20–22] that diethylaluminium chloride, triethylaluminium, ethylbis-2-phenylbutylaluminium, tri-isobutylaluminium, ethylaluminium dichloride, and also titanium tetrachloride and hydrogen chloride cause chemical changes in the polymers accompanied by a diminution in the unsaturation as a result of intramolecular cyclisation. A similar phenomenon is observed in the action of alkylmagnesium halides on a solution of 1,4-polybutadiene[21].

Cyclic polymers of butadiene and isoprene, obtained by direct polymerisation of the monomers in the presence of an alkylaluminium dichloride or titanium tetrachloride[21], have softening points of 420° and 370°C respectively. The cyclopolymerisation of isoprene in the presence of ethylaluminium dichloride has been subjected to a detailed investigation by Kössler et al.[23]

Gaylord and a number of Czechoslovak investigators have published interesting work on the polycyclisation of diene monomers with conjugated double bonds, and also on the cyclisation of stereoregular polymers of dienes[24–27]. Thus by the polymerisation of butadienes, isoprene, and chloroprene with the aid of a Grignard reagent and titanium tetrachloride at molar ratios of Mg/Ti < 2 (especially with Mg/Ti = 0.5–1), and also by the polymerisation of butadiene and chloroprene with triethylaluminium and titanium tetrachloride at molar ratios of Al/Ti ≤ 0.5, Gaylord, Kössler, et al.[24,25] obtained insoluble polymeric powders, whose spectra resembled the infrared spectra of cyclised *trans*-1,4-, *cis*-1,4-, and 3,4-polyisoprenes. These investigators suppose that cyclic structures are formed in the course of polymerisation from 1,2-polymers, not as a result of action by the catalyst on initially formed linear chains. The products obtained, still containing a definite proportion of linear structures, were completely cyclised by the action of sulphuric acid on a suspension of the polymers in toluene.

The following mechanism has been suggested for the cyclopolymerisation of conjugated dienes. Since the metal halide is present in considerable quantity, the polymerisation can be regarded as cationic. The first stage involves 1,2-isotactic or 1,2-syndiotactic polymerisation (3,4-isotactic or 3,4-syndiotactic in the case of isoprene or chloroprene). Initiation of polycyclisation can take place in two ways: (1) the end of a growing chain may interact with a double bond in the penultimate monomeric

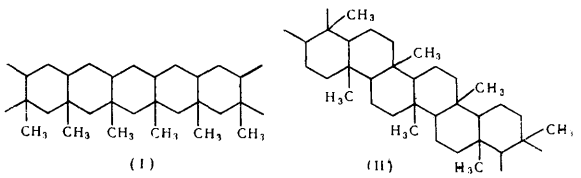
unit (*a*, *c*); or (2) the growing chain may interact with a double bond in another chain (*b*, *d*):



Thus an isotactic polymer yields a planar ladder structure, whereas a syndiotactic polymer gives a spiral structure, one chain being curled around another and joined to the latter at every third carbon atom.

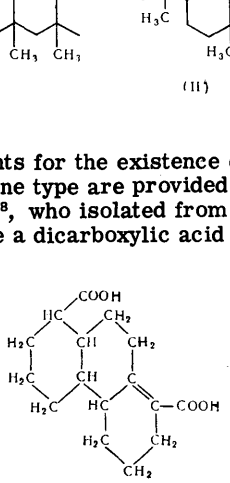
A characteristic feature of cyclopolymers is their high thermal stability. The decomposition temperatures of cyclopolyisoprene, cyclopolybutadiene, and cyclopolychloroprene are respectively[24,25] 370°, 405°, and 422°C.

Kössler et al. concluded[27] from their investigations, which involved mainly a study of the infrared spectra of cyclopolymers of isoprene and cyclised steroregular polymers of isoprene, that polycyclic ladder systems may be of two types—perhydroanthracene (I) and perhydrophenanthrene (II).

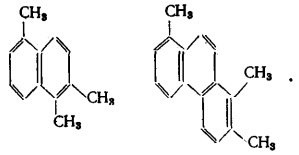


(I) (II)

Definite arguments for the existence of polymers of perhydrophenanthrene type are provided by results obtained by Shelton and Lee[28], who isolated from the oxidation of cyclic polybutadiene a dicarboxylic acid having the structure



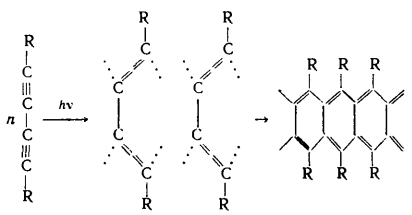
and also by Wallenberger[29], who by the aromatisation of the polymer of isoprene obtained 1,2,5-trimethylnaphthalene and probably 1,2,8-trimethylphenanthrene.



The technical application of cyclised rubber is extremely promising. It can be successfully used as a filler for natural and synthetic rubbers[6,30-32], the properties of the resulting products being improved and the processing technology facilitated. Cyclised rubber is employed for the production of paints[6,32], coatings for paper[6,32] and textiles[32], etc.

2. Aromatic Ladder Polymers

The aromatic ladder polymers obtained by Bohlmann[33,34] by the photopolymerisation of polyacetylenes are of great interest. Thus irradiation of deca-4,6-diyne-1,10-diol $HO[CH_2]_3[C{:}C]_2[CH_2]_3OH$ and also of its diurethane yields insoluble red polymers. If the diurethane is heated below the melting point, a red polymeric product is formed, but on rapid heating above the melting point the compound melts without change in colour and does not polymerise at 250°C. In Bohlmann's opinion this indicates that, for polymerisation to occur, the molecular chains of the polyyne should be arranged in parallel. The polymerisation of a conjugated diyne can then be represented by the scheme



Under the influence of light energy the π-electron pairs of the triple bonds break down, and polymerisation takes place by a Diels–Alder type of synthesis. Reaction takes place only in the crystalline monomer, but not in solution or in the melt.

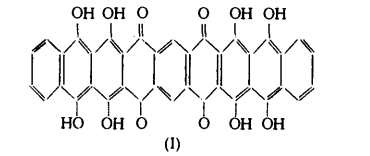
The infrared spectrum of the polymers shows broad peaks in the region of absorption by aromatic hydrocarbons, but neither triple nor isolated double bonds have been detected in the spectrum. X-Ray examination of the polymers indicates that they are amorphous substances[33].

In an attempt to prepare 1,6-dicyanohexa-2,4-diyne, Lee[35] obtained chemically inert polymeric products of high melting point (above 600°C), resembling "brick dust". His starting materials were a dihalogeno-, ditoluene-*p*-sulphonyl-, or dihydroxy-hexadiyne and sodium or copper(I) cyanide. Polymerisation proceeds as follows

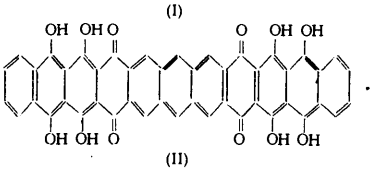
$$X{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}X \xrightarrow[\text{salt}]{\text{cyanide}} [X{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}CN]^{-} \rightarrow \text{polymer.}$$

Although Lee does not attribute a definite structure to this polymer, nevertheless in his view it may contain fused aromatic rings, recalling in this respect the structures of heat-treated polyacrylonitrile or of graphite.

By the interaction of the dianhydrides of aromatic tetracarboxylic acids (pyromellitic and anthracenetetracarboxylic acids) with 1,4-dihydroxyanthraquinol in the presence of aluminium chloride, Marschalk obtained[36] fused polycyclic aromatic systems, to which he ascribed the structures



(I)

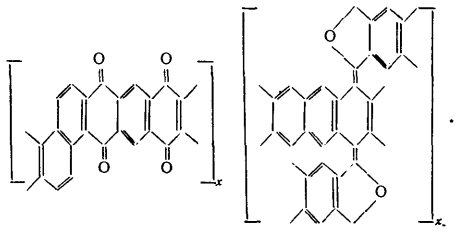


(II)

These compounds were synthesised by heating 1 mole of the dianhydride with 2 moles of the anthraquinol in the presence of a Friedel–Crafts catalyst to 310–320°C. The product (I) is a brown–violet substance, insoluble in alkalis and organic solvents, which can be crystallised from slightly fuming sulphuric acid on gradual dilution. The product (II) likewise does not dissolve in alkalis or organic solvents, and is crystallised in a similar manner to (I).

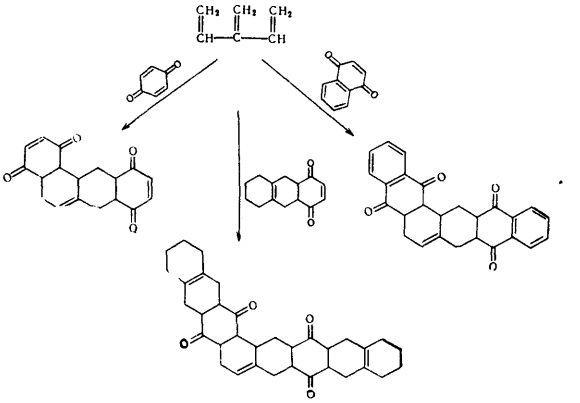
In order to study the mechanism of conduction in semiconductor materials, Pohl and Engelhardt[37] synthesised polymers from various acenes (naphthalene, anthracene, phenanthrene, pyrene, chrysene, perylene, dibenzopyrene, and picene) and aromatic acid anhydrides (phthalic and pyromellitic) in the presence of zinc chloride or aluminium chloride. (Polyacenes were also prepared by the Wurtz–Fittig method from 1,2,4,5-tetrabromobenzene by its interaction with a sodium–potassium alloy.) Pyromellitic dianhydride or phthalic anhydride was carefully mixed with zinc chloride and the various acenes, and heated at 256° or 306°C for 24 h. The resulting polymers were insoluble, infusible black products. Yields were 5–50% based on the mixture of dianhydride and acene. Elementary analysis indicated that the polymers contained approximately 2 molecules of acene for each molecule of pyromellitic dianhydride after allowing for a loss of 2 molecules of water. Polymers containing up to 14 aromatic nuclei could be prepared. It was found that the resistance diminished with increase in the proportion of the initial acene.

In the opinion of Pohl and Engelhardt[37], two reaction mechanisms are possible, one resulting in the formation of keto-groups or quinone groups, whereas the second yields lactone structures—

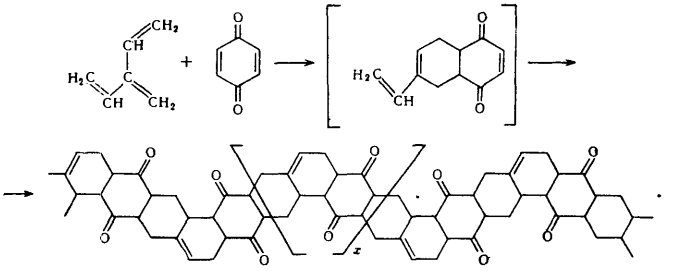


By analogy with the work of many other investigators, however, they consider that the former types of structures are mainly produced, rather than lactone structures, although secondary reactions of the quinone groups are not excluded.

An extremely interesting method for obtaining quinones of hydrogenated acenes has been worked out by Bailey and Economy[38], using 3-methylenepenta-1,4-diene and mono-, di-, and tri-cyclic quinones. Toluene solutions of the hydrocarbon and the quinone are mixed, left at room temperature for 24 h, and then boiled for 24 or 48 h. On cooling, crystalline products separate. The reactions underlying the synthesis of these compounds are



This original variety of diene synthesis has been used somewhat later for the preparation of ladder polymers[39] from 3-methylenepenta-1,4-diene and benzoquinone in equimolecular proportions: a chloroform solution of the mixture was kept at room temperature for 4 days, and then boiled for 24 h, after which most of the solvent was distilled off and boiling continued in the presence of tetrachloroethane for 48 h, until a brown deposit was formed. Two products—a polymer softening at 340–400°C, practically insoluble in all solvents in the cold, but soluble in hot solvents, and probably having a molecular weight of ~ 2000; and a soluble polymer, softening at 170–200°C, and of molecular weight 440—were obtained, the first of these polymers being assigned the following ladder structure[39]



B. HETEROCYCLIC LADDER POLYMERS

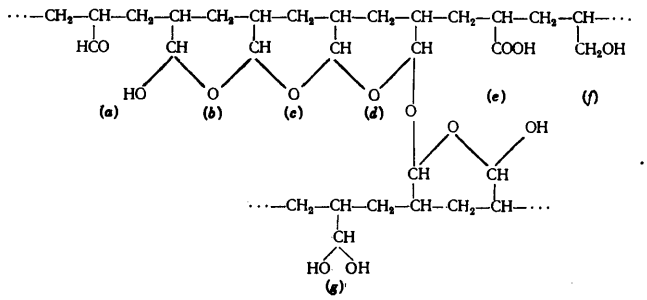
Heterocyclic ladder polymers constitute a group of numerous compounds of high molecular weight. Their macromolecules contain heterocycles comprising carbon atoms together with one, two, or more atoms of other elements, e.g. oxygen and nitrogen. Many organoelementary and inorganic polymers, either containing no carbon at all or containing it only in side-chains, are of the same type.

1. Ladder Polymers Consisting of Oxygen Heterocycles

Polyacrylaldehyde, obtained by the spontaneous polymerisation of acrylaldehyde, was first described by

Redtenbacher[40] in 1843. The polymer was termed "disacryl". The "disacryls" are colourless substances, either flocculent or powdery, having no definite melting point and decomposing at temperatures above 220°C.[42]

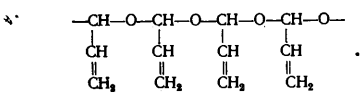
A systematic investigation of the polymers formed by acrylaldehyde was made by Schulz[41]. The polyacrylaldehydes which he obtained by a radical mechanism, as well as those formed by spontaneous polymerisation (also proceeding by a radical mechanism), were polymers of vinyl type, with a "head-to-tail" structure. However, the formyl groups in the polymers can interact to form rings. From the chemical properties and the infrared spectra Schulz attributes to such polymers the structure[41]



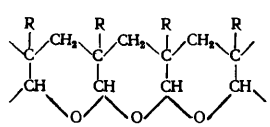
The formyl groups may be present either in the free state (*a*), hydrated (*g*), in ethereal form (*c*), or in an intermediate form (*b*). The hydroxyls of the hydrated formyl groups are able to form cross-links (*d*). Under certain conditions they break down, the polymers acquiring solubility and reacting as polyals.

In the presence of metallic sodium, the polymerisation of acrylaldehyde in boiling benzene takes place in the 1,4-positions, as Andreeva and Koton[43] have shown.

According to Schulz[44] the polymerisation of acrylaldehyde in the presence of various anionic catalysts and the boron trifluoride–ether complex results in a polymer having the structure

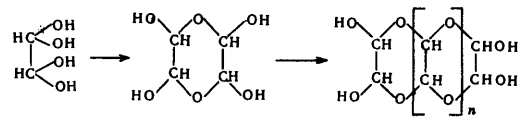


Andreeva et al.[45] polymerised acrylaldehyde and methacrylaldehyde in the presence of respectively ~ 1.5 and 2.5–3 mole % of boron trifluoride at temperatures from −20° to −40°C. The vitreous polyacrylaldehyde obtained under these conditions contained no detectable free formyl groups. It was insoluble in organic solvents, it dissolved in sulphurous acid, and it decomposed at about 270°C. The polymethacrylaldehyde had rather greater thermal stability than the acrylaldehyde polymer, and differed from the latter in being insoluble in most organic solvents and only swelling in sulphurous acid. In view of their properties, these polymers were assigned[45] the polycyclic structure



where R = H or CH_3.

The polymerisation of glyoxal yields a white solid, aqueous solutions of which comprise a mixture of hydrated forms capable of changing from one into another[46,47]:



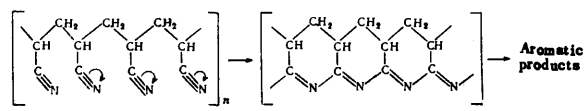
where n = 3 or 4. Okamura et al.[48] investigated the polymerisation of glyoxal under the influence of γ-rays at −196°, −78°, and 0°C, obtaining degrees of conversion of 23.9%, 42.2%, and 60.6% respectively after irradiation for 65 h. The infrared spectra of the polymer showed absorption corresponding to C–O–C and C–H bonds, but no absorption due to the carbonyl group. The polymers were distinguished by infusibility and insolubility. At 222°C some 45% of the polymer had decomposed after 10 min.

2. Ladder Polymers Consisting of Nitrogen Heterocycles

Most investigators consider that a ladder type of polymer is formed by the heat-treatment of polyacrylonitrile. A fair number of papers have been published on the thermal transformation of polyacrylonitrile and the properties of the products, and only a proportion of these will be briefly discussed in the present review.

Houtz[49] heat-treated polyacrylonitrile fibre, and obtained a thermostable material which withstood brief heating in the burner flame. He was the first to ascribe a polycyclic structure to it.

Burlant and Parsons[50] heated samples of polyacrylonitrile in an atmosphere of nitrogen over a range of temperatures from 200° to 320°C, and investigated their infrared spectra. The process of polycyclisation was represented as follows:

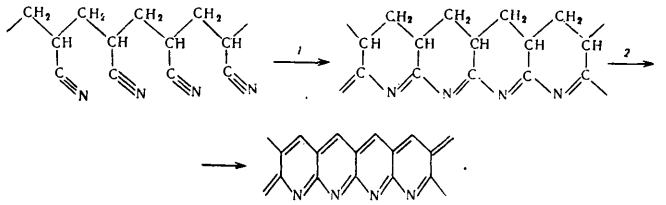


This scheme explains the high nitrogen content of the heated polymer and the gradual, almost complete disappearance of nitrile groups, with the simultaneous appearance of conjugated C=N bonds. Aromatisation occurs slowly below 300°C, whereas at higher temperatures aromatic products are readily formed.

Topchiev et al.[51] showed that heat-treatment of polyacrylonitrile fibre or powder may yield materials possessing semiconductor properties and electronic conduction. The number of electrons having unpaired spins in the substance is 10^{18}–10^{19} g^{-1}. After heat-treatment the semiconductor material can be used at far higher temperatures than, for example, germanium, since the polymer does not decompose even at 300°C. Preliminary exposure of polyacrylonitrile to γ-rays followed by heat-treatment leads to a sharp increase in the concentration of electrons with unpaired spins in comparison with the unirradiated polymer.

From a study of the infrared absorption spectra Topchiev and his collaborators[52] consider that the thermal

transformation of polyacrylonitrile takes place in two stages:



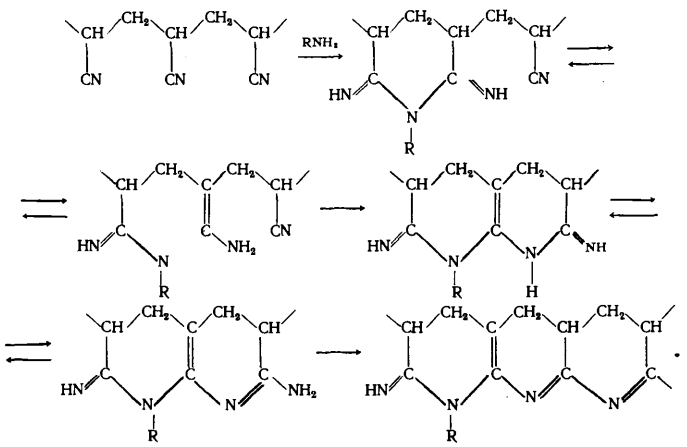
Intramolecular cyclisation, resulting from conversion of a C≡N into a C=N bond, is mainly completed by 270°C. At higher temperatures dehydrogenation takes place, with the formation of C=C bonds. The conditions of heat-treatment have a great effect on the electrical properties of the semiconductors. Thus heat-treatment of polyacrylonitrile in ammonia under pressure increases its conductance by factors of the order of 10^2 in comparison with specimens which have been subject to the same heat-treatment but in an atmosphere of an inert gas.

Vosburgh[58] made a detailed study of the conditions required for the production of non-flammable cyclised polyacrylonitrile fibres and fabrics. He heated the polymer in air above 160°C, and established that the logarithm of the reaction time is inversely proportional to the temperature. The most important parameters in this process are the duration of heating, the temperature, the fabric construction, and the atmosphere in which reaction occurs. The optimum concentration of oxygen is 15–20%. The cloth obtained in this way considerably surpasses all others in thermal stability. At 900°C the material is completely destroyed in 3 h.

Drabkin et al.[54] investigated the processes occurring in polyacrylonitrile on heating. They studied the absorption spectra after heating in a vacuum of 10^{-5}–10^{-6} mmHg.

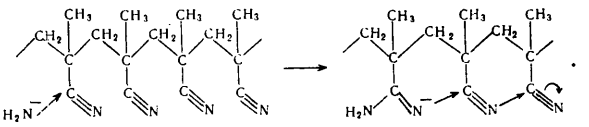
Airapetyants et al.[55] investigated the temperature dependence of the electrical properties of polyacrylonitrile (in a vacuum of 5×10^{-6} mmHg) for specimens of the polymer which had been heat-treated from 520° to 730°C.

Many authors[56-61] consider that the coloration of polyacrylonitrile and polymethacrylonitrile is caused by the formation of fused polycyclic systems. This process is accelerated by the presence of bases or organic acids. Thus La Combe[56] found that heating polyacrylonitrile in the presence of a small quantity of a base at 100°C for 1 h results in the appearance of a yellow colour in the polymer. He explains this phenomenon by means of the suggested scheme



Dilute mineral acids hydrolyse the fused rings, with almost complete disappearance of the colour[56].

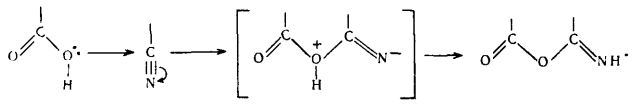
Overberger et al.[57] investigated the polymerisation of methacrylonitrile in the presence of lithium and ammonia at −75°C. The appearance of a colour in the polymer was, in their view, due to the reactions



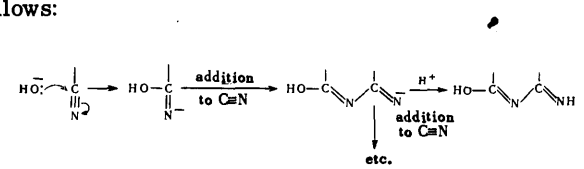
Chain growth occurs by interaction of an imino-anion with a nitrile group.

Lipatnikov[58] also explains the coloration of polymethacrylonitrile, when the monomer is polymerised in the presence of benzoyl peroxide under pressure (6000 kgf cm^{-2}) at or above 100°C, by the formation of fused pyridine rings.

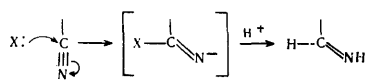
From an investigation of the appearance of a colour in polymethacrylonitrile[59-62] and polyacrylonitrile[62], Grassie concluded that this process is in considerable measure bound up with the presence of carboxy-groups, which initiate polymerisation:



Carboxyls are usually present in the polymer, since the monomer contains methacrylic acid as impurity. However, other compounds, not necessarily located in the polymer chain, can also initiate cyclisation[60]. The efficiency of initiation by acids of the type RCOOH is then strongly dependent on the nature of R: the more strongly developed the electron-acceptor properties of R, the more difficult is initiation[61]. An analogous relationship is observed with phenols. Initiation by alkalis occurs as follows:



In summarising the results of observations on the change in colour in polymethacrylonitrile and polyacrylonitrile, Grassie[61] gives the general mechanism



for the initiation of polycyclisation. Thus the start of the reaction is reduced to attack on a nitrile group by a nucleophilic reagent. Here OH, NH_2, etc. are stronger nucleophilic reagents, and carboxylic acids and phenols less strong. All these compounds are in essence Lewis bases.

While noting much in common in the behaviour of polyacrylonitrile and polymethacrylonitrile on heat-treatment, Grassie[62] nevertheless points out two fundamental differences. Firstly, in the absence of nucleophilic reagents polymethacrylonitrile does not change colour below 200°C,

whereas pure polyacrylonitrile becomes coloured at a definite rate, which does not decrease after careful purification of the monomer. This fact is explained by the presence in the polyacrylonitrile molecules of hydrogen atoms attached to tertiary carbon atoms, which are capable of initiating polycyclisation. Polymethacrylonitrile molecules, however, do not contain the $\geq$C–H group. Secondly, even intensely coloured polymethacrylonitrile does not lose its solubility, whereas polyacrylonitrile rapidly becomes insoluble. The explanation given for this is that in the latter polymer the process of chain growth takes place by the cross-linking of the latter (propagation cross-linking) owing to the denser packing of the macromolecules [62].

Kennedy [63] considers that, besides the ionic reactions which accompany the heat-treatment of polyacrylonitrile, radical processes must also be considered.

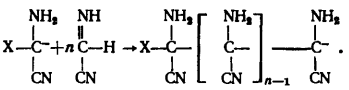
Nizova et al. [64] have synthesised a polyacetylenenitrile whose structure does not essentially differ from that attributed to heat-treated polyacrylonitrile. The polymer obtained is a dark coloured powder, insoluble in the usual organic solvents and readily soluble in concentrated acids. It neither melts nor decomposes up to 450°C, and is distinguished by a narrow electron spin resonance (e.s.r.) signal, which is characteristic of polyconjugated systems. The number of unpaired electrons is 10^{18}–10^{19} g^{-1}. The infrared spectra support the structure proposed for the polymer, and contain an absorption band characteristic of polyconjugated C=N bonds. They indicate that prolonged heating in a vacuum up to 300°C has practically no effect on the chemical structure of the polymer.

The literature on the polymer of hydrocyanic acid was reviewed by Völker [65], who synthesised this polymer by anionic polymerisation in aqueous solution. Polymeric hydrocyanic acid consists of dark brown amorphous flakes, which do not dissolve in any solvent without chemical change. Ammonia is eliminated by the action of aqueous alkali, and gaseous compounds of nitrogen are formed by concentrated nitric acid. The polymer possesses limited solubility in other dilute mineral acids. It is thermally stable up to 200°C, but at higher temperatures hydrogen cyanide, ammonia, carbon dioxide, and an amine are split off.

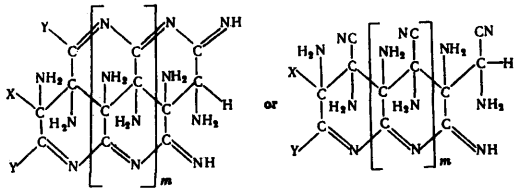
Polymerisation is initiated by interaction of an anion with the dimer of hydrocyanic acid:

$$X^- + HN{=}CH{-}CN \rightarrow H_2N{-}\overline{C}(X){-}CN.$$

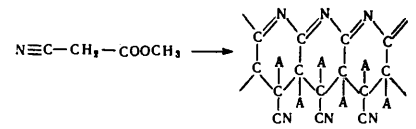
Chain growth proceeds by interaction of the dimeric acid with the resulting anion:



Chain termination results from addition of a cation (usually a proton) to the polymeric molecule. Völker [65] considers that, owing to steric hindrance, the nitrile groups occupy *trans*-positions in the course of polymerisation, which leads to formation of the polycyclic structures

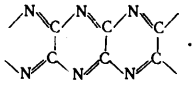


Korshak and Sosin [66] prepared a polymer from methyl cyanoacetate by polyrecombination:



where A = $COOCH_3$. Polyrecombination is accompanied by polymerisation of the nitrile groups with formation of a system of conjugated C=N bonds in fused six-membered rings. The infrared spectra of the polymer exhibit absorption characteristic of C=N bonds, and also of nitrile and ester groups. The molecular weight of the polymer is 7200, and its softening point 500°C. The product possesses semiconductor properties. A signal is observed in the e.s.r. spectra (7 oersteds), and the number of electrons having unpaired spins is 10^{18} g^{-1}. An analogous structure (with fused nitrogen heterocycles) is possessed also by polymers based on malononitrile [67], adiponitrile [67,68], and benzyl cyanide [67], as well as copolymers of methyl cyanoacetate and benzyl cyanide [69].

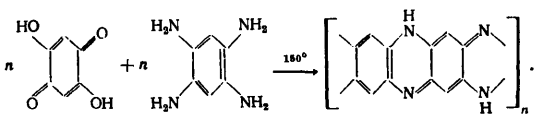
Bircumshaw [70] published a survey of work on polymers of cyanogen $(CN)_2$ obtained in various ways, and reported the synthesis and a study of the properties of a polymer, paracyanogen, formed by the polycondensation of oxamide in the solid phase under pressure at 250–300°C. Paracyanogen contains conjugated double bonds and no free nitrile groups. The polymer molecules consist of fused pyrazine rings



Paracyanogen is insoluble in water and most organic solvents, but soluble in inorganic acids. The polymer withstands being heated in a vacuum at 450°C. Strong heating in air leads to decomposition with the formation of carbon dioxide. Davydov et al. [71] investigated the temperature dependence of the semiconductor properties of paracyanogen.

Several polymers containing a conjugated system of C=N groups have been obtained by Paushkin et al. [72] from amides and ammonium salts of mono- and di-carboxylic acids heated in the presence of zinc chloride in an autoclave (at 400°C). The polymers were insoluble, infusible powders, from dark brown to black in colour. They possessed very high thermal stability: the losses in weight on heating to 800°C were only 7–12%. The infrared spectra of these products are identical with those of polymers obtained by polymerisation of the corresponding nitriles. The electrical properties of the polymers were examined over the range 20–300°C.

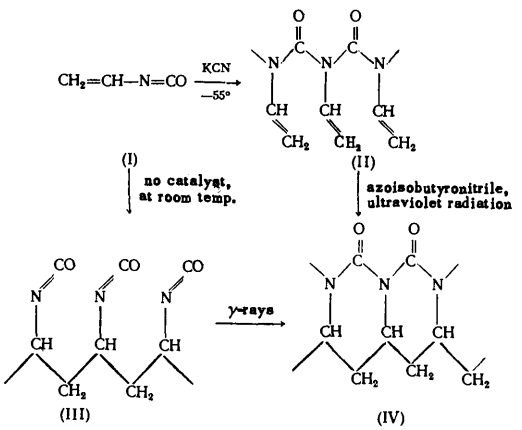
By heating equivalent amounts of 2,5-dihydroxy-*p*-benzoquinone and benzene-1,2,4,5-tetra-amine in dimethylacetamide, hexamethylphosphoramide, or polyphosphoric acid at 150°C, Stille and Mainen [73] have quite recently obtained ladderlike polyquinoxalines:



With dimethylacetamide the polymers form extremely stable compounds, which decompose only on prolonged

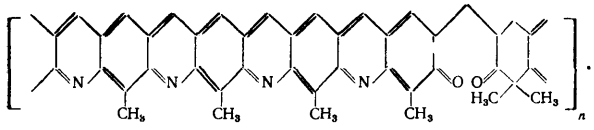
heating in a vacuum. Removal of solvent from the association complex results in an insoluble polymer. Thermogravimetric tests showed that the structure of the polymer is evidently not completely ladderlike.

Overberger et al.[74] obtained a ladder polymer of vinyl isocyanate by the series of reactions

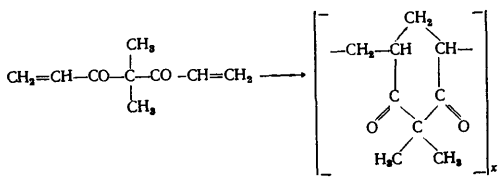


The polymer (IV) is soluble in solvents of high dielectric constant. The intrinsic viscosity of its solution in pyridine is 0.45. The polymer decomposes at 385–390°C. The structures of the intermediate products (II) and (III) and of the polymer (IV) have been demonstrated by means of the infrared spectra.

De Winter and Marvel[75] synthesised a ladder polymer whose molecules were made up of fused alternating aromatic pyridine and toluene rings:

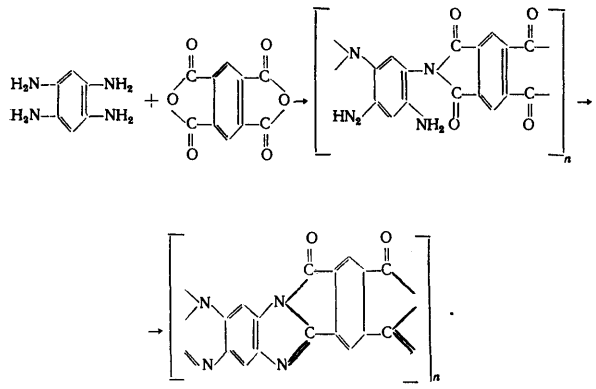


Polymerisation in a solution of 4,4-dimethylhepta-1,6-diene-3,5-dione in the presence of azoisobutyronitrile at 65°C first yielded a polymer containing six-membered rings in the chain:

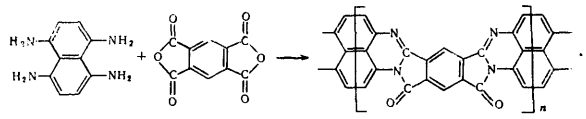


Then hydroxyimino-groups (approximately one group for each ring) were introduced into it in strongly alkaline medium. Careful dehydration of the polyoxime yielded a ladder polymer (whose structure has been given above), soluble in hot quinoline, dimethyl sulphoxide, and dimethylacetamide. Thermogravimetric tests showed that the loss in weight of the polymer on being heated from 300° to 500°C was ~ 20%, after which only a slight change in weight was observed right up to 900°C.

Novel thermostable ladder polymers have recently been obtained based on aromatic tetra-amines and aromatic tetracarboxylic acids or their dianhydrides[76–80]. Dawans and Marvel[76] have synthesised such polymers from benzene-1,2,4,5-tetra-amine and pyromellitic dianhydride:



They also replaced the benzenetetra-amine by naphthalene-1,4,5,8-tetra-amine for the polycondensation:



These workers observed with model compounds that the nature of the intermediate products depends on the conditions of the condensation, and concluded that, in order to obtain the above ladder structures, the process must be carried out with a slow rise in temperature (2 deg min^{-1}). The polycondensation was conducted in a melt or a solution in a stream of nitrogen[76]. Reactions begins in the melt at 105–110°C, but intramolecular cyclisation takes place only at 140–150°C. Polymers of maximum molecular weight are obtained with the starting materials in equimolecular proportions: when the molar ratio of anhydride to amine exceeded unity, the yield of the polymer was higher, but its molecular weight lower.

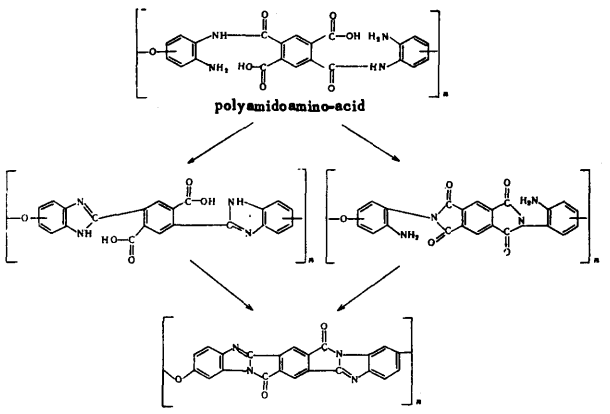
The polymer based on benzene-1,2,4,5-tetra-amine was prepared by gradually heating a mixture of the amine with the dianhydride to 220°C, and then heating in a vacuum at 300°C for 3 h. The yield was 86%. The reduced viscosity of a 0.25% solution in concentrated sulphuric acid was 0.3. Use of polyphosphoric acid as solvent for the synthesis of this polymer[76] makes it possible to employ the stable tetra-amine tetrahydrochloride instead of the readily oxidisable amine, and also gives the same yield (86%) of polymers of high molecular weight. The intrinsic viscosity of the polymer based on benzene-1,2,4,5-tetra-amine, measured in concentrated sulphuric acid, was 1.10.

The polymer based on naphthalene-1,4,5,8-tetra-amine was obtained in 60% yield in 2,5,8-trioxanonane solution. The reduced viscosity of a 0.25% solution in concentrated sulphuric acid was 0.41.

It was established that in a solvent the reaction between tetra-amine and dianhydride occurs essentially at room

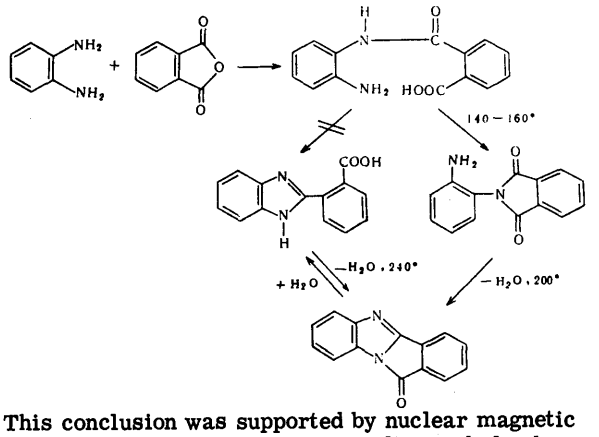
temperature and is weakly exothermic. A polyamido-amino-acid is formed as intermediate product [77,78].

Scheme 1



On the basis of infrared spectroscopic data Bell [78] suggests Scheme 1 for ring formation in the interaction of pyromellitic dianhydride with bis-3,4-diaminophenyl ether. According to this both imide and benzimidazole rings are formed in the cyclisation of the polymeric amido-amino-acid. In a study of the condensation of *o*-phenylenediamine with phthalic anhydride when they were heated at 160°C for 30 min, Colson et al.[79] found that only a phthalimide ring is formed, and no benzimidazole ring formation is observed (see Scheme 2).

Scheme 2

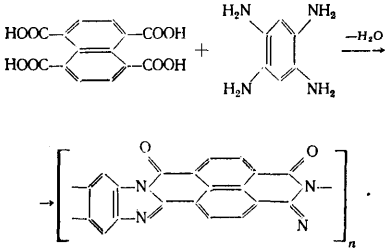


This conclusion was supported by nuclear magnetic resonance and infrared spectral results, and also by a comparison of the melting point of *N*-*o*-aminophenylphthalimide with published values. The imide obtained is converted, when heated to 200–210°C, into benzoylbenzimidazole (see Scheme 2). This last product cannot be formed from *o*-benzimidazol-2-ylbenzoic acid below 240–250°C, which provides additional evidence for the scheme of cyclisation given by Colson et al.[79]

Ladder polymers of this type, termed "pyrrones" [77], are coloured substances, which do not melt below 400°C. They are not soluble in the usual organic solvents, but dissolve in concentrated sulphuric acid [76]. Thermogravimetric tests have shown that in an inert atmosphere (nitrogen) pyrrones are thermostable up to 450–500°C. In air they oxidise fairly rapidly at 350–400°C, [76] but they are non-flammable. Pyrrones are extremely resistant to the action of radiation [78].

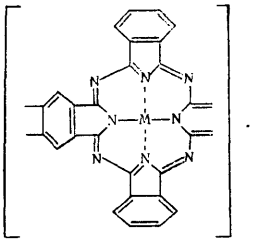
The possibility of obtaining soluble intermediate products in the synthesis of pyrrones facilitates the technical production of thermostable films, coatings, adhesives, filaments, and plastics based on them [77,78].

By the polycondensation of naphthalene-1,4,5,8-tetracarboxylic acid with benzene-1,2,4,5-tetra-amine in polyphosphoric acid, the system being heated in an atmosphere of nitrogen at 220°C, van Deusen [80] obtained novel thermostable polymers, closely resembling pyrrones in structure:



In contrast to pyrrones, however, the imide ring of these polymers is six-membered. They are dark coloured products, partly soluble in sulphuric, polyphosphoric, and sulphonic acids, and also in aqueous alkalis. The polymer obtained at ~ 100°C has a reduced viscosity of 0.3. Polymers obtained at higher temperatures are very sparingly soluble, but have analogous infrared spectra. These products are distinguished by very great thermal stability: on heating in air, loss in weight does not begin below 400°C, and in nitrogen at about 600°C.

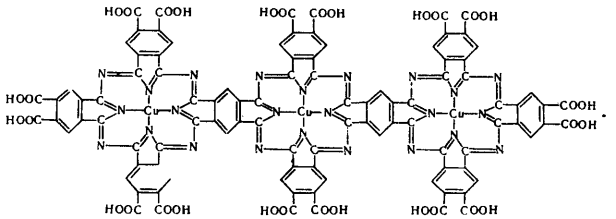
Phthalocyanine polymers have now been synthesised which are characterised by the presence of complicated polycyclic structures containing nitrogen. Individual members of this group are able to form ladder systems. Thus Marvel [81] heated pyromellitic acid, phthalic anhydride, urea, and copper(II) chloride to 200°C, and obtained polymers which may have the structure



The polymers vary in colour from bluish green to greenish black. They are soluble in dimethylformamide, they are stable when heated in air to 350°C, and they burn with great difficulty.

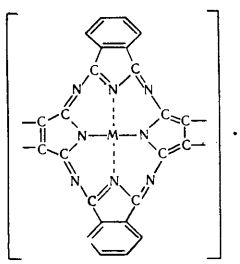
Soluble phthalocyanine polymers were prepared by Felmayer and Wolf [82] and also by Berlin et al.[83] by the polycondensation of pyromellitic acid with urea and copper(I) chloride. Felmayer investigated the electrical properties of these black products, and found that the activation energy for conduction diminished with increase in the number of fused rings in the polymers. Berlin's polymers were blue-green powders, with molecular weights of 3000–4000, and were insoluble in dimethylformamide but soluble in concentrated sulphuric acid. The magnetic and electrical properties of these polymers were examined, as well as their thermal stability. The number of paramagnetic particles was 5×10^{21} g^{-1}. The polymers were stable in air up to 350°C.

Drinkard and Baylar[84] prepared phthalocyanine polymers from pyromellitic dianhydride, urea, copper(II) chloride, and a catalyst (ammonium molybdate or $ZrOCl_2 \cdot 8H_2O$) at 180°C, and attributed to them the structure



The maximum molecular weight of the polymers obtained was 4000, corresponding to six phthalocyanine units.

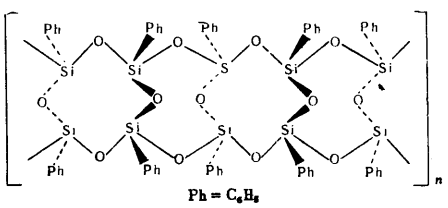
Berlin et al.[85] showed that the interaction of an equimolecular mixture of copper acetylacetonate, tetracyano ethylene, and phthalonitrile yields a chelate copolymer, which probably has the structure



3. Organoelementary Ladder Polymers

In 1939 Koton[86] reported the preparation of organosilicon polymers by the polycondensation of phenyl-, benzyl-, and also 1-naphthyl-silanetriol. These polymers were recommended for use as heat-resistant materials for electrical insulation.

By the equilibrium alkaline polycondensation of phenylsilanetriol, in toluene, xylene, or 2,5,8-trioxanonane, Brown et al.[87] have fairly recently obtained ladder polymers, to which they assign the structure



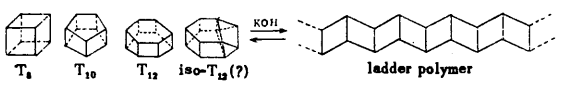
Ph = C_6H_5

The polymer obtained by the hydrolysis of phenyltrichlorosilane followed by polycondensation in toluene had $\overline{M}_n = 14\,000$ and $\overline{M}_w = 26\,000$, with a "most probable" molecular-weight distribution. A steep linear relationship ($a = 0.92$) exists between values of $\lg[\eta]$ and $\lg\overline{M}_w$ for fractions of this polymer, this being characteristic of a rigid elongated polymer. By using small amounts (e.g. 5–30%) of solvent, a polymer can be obtained having a molecular weight of the order of several millions. With $\overline{M}_w > 2 \times 10^5$, however, chain branching is observed[87]. Analogous products were synthesised by Sprung and Guenther[88] by the hydrolysis of phenyltriethoxysilane. These products had a somewhat higher molecular weight and a narrower molecular-weight distribution than the polymer synthesised by Brown.

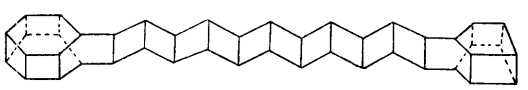
Brown considers[89] that the trifunctional product forms initially a syndiotactic Si–O–Si chain having phenyl side-groups attached to each silicon atom. This chain then reacts with another chain, to form the "unidimensional" ladder structure shown above.

From a detailed study of the influence exerted by the equilibrium conditions on the nature of the products, Brown[90] showed for the polycondensation of phenylsilanetriol that in dilute (5%) solutions oligomers of cagelike structure are formed, in 5–70% solutions a linear ladder polymer of low molecular weight, at 85–95% a ladder polymer of high molecular weight, and at 100% a ladder gel. All these products are interconvertible by varying the concentration in the solution.

The equilibrium between the oligomers and the polymer can be represented in general as follows:



where $T = RSiO_{1.5}$. The phenyl derivatives T_8, T_{10}, and T_{12} have been isolated as pure crystals. Since the product of low molecular weight contains no unchanged silanolic groups, while the spectra confirm the presence of rings similar to T_{10} or T_{12} at the ends of the chains, the polymer was given the structure



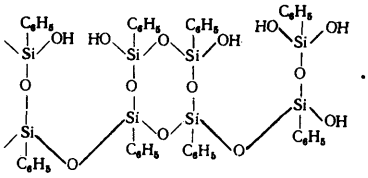
Raising the equilibrium temperature results in an increase in the proportion of cagelike compounds. At 250°C and a polymer concentration exceeding 80%, branchings appear in the macromolecules, accompanied by a decrease in the concentration of cagelike compounds.

From a study of the properties of the solutions, X-ray examination of oriented specimens, determination of the infrared and ultraviolet spectra, and calculations of bond angles, Brown[87,90] concluded that the product of the polycondensation of phenylsilanetriol is a ladder polymer having a *cis*-syndiotactic structure of the double bond.

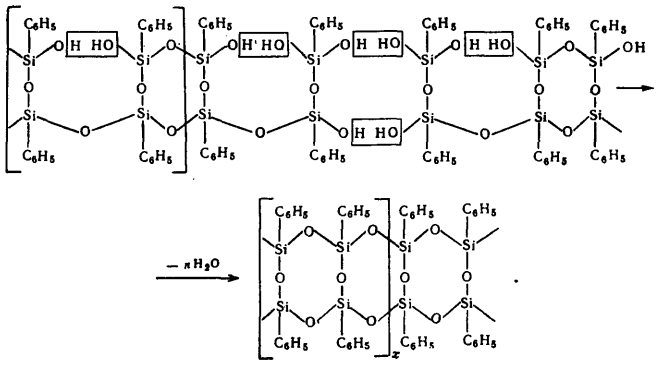
The above organosilicon ladder polymers have been investigated also by Pavlova et al.,[91,92] who used benzene, toluene, xylene, and succinonitrile as solvents for the synthesis. All the polymers obtained, having high glass points (~ 300°C), were divided into 6–10 fractions. The closely similar glass points for all four polyphenylsiloxanes indicate that the conditions of preparation have no fundamental effect on their structure. These conditions likewise have little influence on the degree of polydispersity of the polyphenylsiloxanes: thus in the series—benzene, toluene, xylene, and succinonitrile—the ratio M_w/M_n has the values 1.82, 2.15, 2.50, and 2.70 respectively.

The suggested mechanism[91] for the formation of ladder polyphenylsiloxanes involves the initial production, by the

hydrolysis of phenyltrichlorosilane, of polymers of low molecular weight, containing free hydroxyls:



followed by further intramolecular and intermolecular condensation:



Polyphenylsilsesquioxanes have been obtained also by Andrianov et al.[93] by polymerising the crystalline octamer $(C_6H_5SiO_{1.5})_8$ in a solvent (diphenyl oxide, nitrobenzene, etc.) in the presence of 0.05% of an alkali, and then removing the solvent and heating at 250–270°C. The polymers have glass points above 300°C.

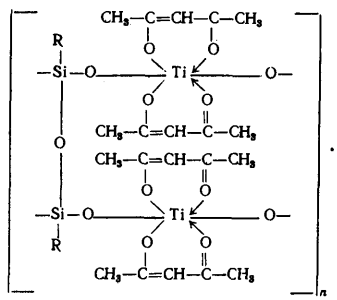
Study of the properties of dilute benzene solutions of polyphenylsilsesquioxanes has shown[92] that at molecular weights of 10 000–50 000 the polymers are present in the form of short rods, whereas over the range 50 000–2 700 000 they exist as tangles of thread. The relation between the intrinsic viscosity and the molecular weight of the polymers is given by

$$[\eta] = 1.305\times10^{-7}M^{1.29} \quad (M = 10\,000 - 50\,000);$$
$$[\eta] = 1.93\times10^{-4}M^{0.634} \quad (M = 50\,000 - 2\,700\,000).$$

The mean square distances between the ends of the macromolecular chains and the flexibility of the chains have also been calculated.

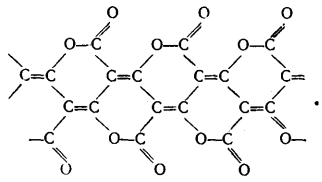
Ladder polyphenylsiloxanes are infusible products, which can dissolve, however, in benzene, tetrahydrofuran, chloroform, and dichloromethane[87,89]. Films can be obtained from the solutions, and these can be oriented in the swollen state. The polymers are more stable towards hydrolysis than are ordinary silicones, and they have a higher tensile strength than have silicones of iregular structure (281–422 kgf cm^{-2}). They possess very good dielectric properties and high thermal stability. Losses in weight are observed at temperatures above 525°C. The polymer withstands brief (1–2 min) heating at 650°C, and several months at 300°C.[90]

Hydrolysis of compounds of type $RSiCl_3$ together with bisacetylacetonatotitanium dichloride yields[94] ladder polymers containing cyclic titanium atoms.

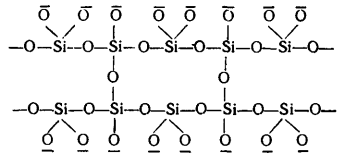


4. Inorganic Ladder Polymers

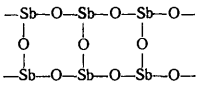
Smith et al.[95] obtained variously coloured—from yellow to violet—polymers of carbon suboxide C_3O_2. The polymers of low molecular weight dissolved in water and aqueous alkali to give red solutions; those of high molecular weight were insoluble. The polymers decomposed above 300°C, and at 500°C were converted into carbon. In Smith's opinion, these products have the structure



Inorganic polymers having molecules or ladderlike structure are quite often encountered in Nature. For example, the mineral tremolite, of which asbestos is a variety, contains amphibole chains[96]:



One form of antimony oxide, valentinite, also has a ladder structure[97]:

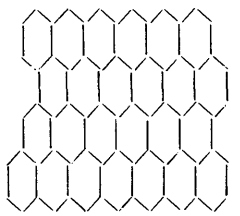


Arsenic sesquioxide[98] and bismuth sesquioxide[99] have similar structures.

II. PARQUET POLYMERS

A typical representative of polymers having a parquet type of structure is graphite. It consists of fused six-membered carbon rings, the distance between the carbon

atoms in them being 1.42 Å, close to the corresponding length in the benzene molecule[100,101]:



The planar networks of carbon atoms form parallel layers, 3.38 Å apart. Graphite is formed in Nature by reducing processes at high temperatures[102]. The graphite layers readily separate from one another, so that this polymer is used in the manufacture of pencils and antifriction materials. The refractoriness and ability to conduct an electric current make it possible to employ graphite for the manufacture of crucibles and electrodes and in foundry work[103].

Graphite can be prepared artificially. Thus flexible fibres and fabrics containing up to 99.9% of graphite have been obtained[104,105] by heating viscose rayon fibre in conformity with the following scheme:

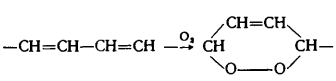
$$\underset{\text{viscose rayon fibre}}{(C_6H_{10}O_5)_x} \xrightarrow{800^\circ} \underset{\text{carbon fibre}}{(C_{36}H_5O)_x} \xrightarrow{3000^\circ} \underset{\text{graphite fibre}}{(C_{28}H)_x}$$

A carbonised fibre containing 90–91% of carbon is first formed, then on further heating a carbon fibre (91–98% of carbon), and at ~ 3000°C the graphite fibre (> 98% of carbon). Carbonisation and graphitisation are complicated processes, which occur when various carbonaceous materials are gradually heated without access of air (up to 3000°C). Practically any textile material can be converted into graphite.

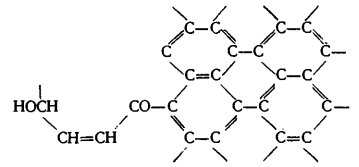
Graphitised fibres are used for reinforcing thermostable plastics, and for manufacturing corrosion-resistant equipment and thermal insulation. Phenolic plastics reinforced with graphite fabric and silicon dioxide fabric can be used for the manufacture of rocket nozzles[104,106].

Winslow et al.[107] investigated the pyrolysis of a 48% divinylbenzene–ethylvinylbenzene copolymer. On heating to 960°C the yield of carbon product was only 6% on the weight of the initial copolymer. Preliminary oxidation (to a content of 18% of oxygen in the polymer), however, leads to a sharp increase in the yield of carbonaceous product (47% calculated on the oxidised copolymer). The pyrolysis of the chlorinated polymer (45% of chlorine) up to 1000°C gives a 55% yield of carbonaceous residue. In Winslow's opinion graphitelike structures are ultimately formed as a result of the thermal changes undergone by the copolymer.

By oxidising conjugated polyenes Berlin and his collaborators[108,109] obtained polymeric peroxides:

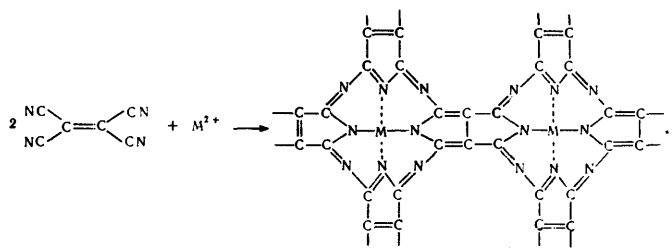


which on being heated over the range 200–300°C underwent complicated chemical reactions resulting in the elimination of water, carbon dioxide, alcohols, ketones, unsaturated hydrocarbons, and benzene with the formation of fused aromatic systems containing up to 15% of oxygen



This polymeric product possessed paramagnetic and semiconductor properties.

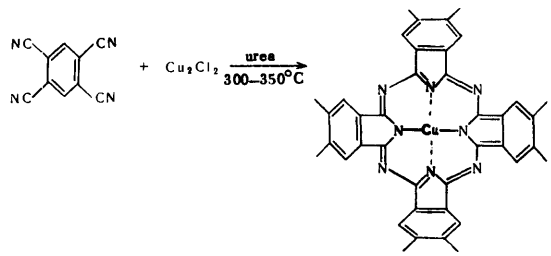
A parquet polymer was obtained by Berlin et al.[85] in the reaction of copper acetylacetonate with two molecules of tetracyanoethylene under vacuum at temperatures from 160° to 300°C:



The polymer was an infusible black product, insoluble in organic solvents, alkalis, and dilute acids. The polymeric chelate complexes of tetracyanoethylene are crystalline and chemically stable; they do not burn, and withstand prolonged heating at 500°C without degradation[110,111]. These products possess semiconductor properties. Analogous polymeric compounds have been obtained using iron and magnesium[112].

Berlin and Matveeva[113] synthesised polymers of tetracyanoethylene also in the absence of metals or their salts. These polymers were regarded as close to the polymeric metal complexes in structure (azaporphyrin rings). When heated in a vacuum (1–2 mm) at 200°C for 200 h, the polymer is probably stabilised, and losses in weight produced by raising the temperature to 350°C reach only 9.6%. Further rise in temperature causes appreciable degradation. The electrical properties of polytetracyanoethylenes and of polychelates of tetracyanoethylene are analogous.

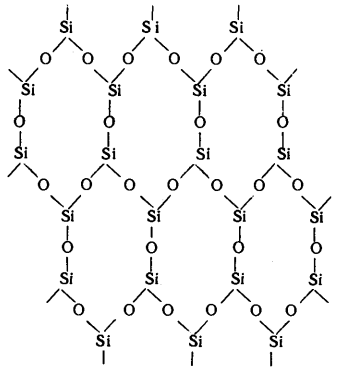
Epstein and Wildi[114] examined the electrical properties of the polymer of copper phthalocyanine obtained by heating the tetranitrile of pyromellitic acid with copper(I) chloride and urea:



The polymer is a purple-black powder. When it is heated in a vacuum (0.25 mm) at 410°C for 18 h, the loss in weight is 10.8%.

A considerable number of parquet polymers are found among the silicates. All silicates are based on the tetrahedral silicon atom combined with four oxygen atoms

located at the vertices of the tetrahedron. Coupling such tetrahedra together may yield the layer structure



in which each silicon atom is attached to an oxygen atom (not shown in the diagram) located either above or below the silicon atom on the normal to the plane of the diagram.

An example of the layer silicates of magnesium is talc, whose composition corresponds to the formula $Si_8O_{20}Mg_6(OH)_4$ or $Mg_3(Si_4O_{10})(OH)_2$. The structure of this mineral can be represented schematically as

$$\begin{matrix} 6\,O \\ 4\,Si \\ 4\,O+2\,(OH) \\ 6\,Mg \\ 4\,O+2\,(OH) \\ 4\,Si \\ 6\,O \end{matrix}.$$

In this polymer two layers of silicon–oxygen tetrahedra are linked together by a "brucite" layer, which consists of $Mg(OH)_2$ and is located between them. The vertices of the tetrahedra in the two silicon–oxygen layers point towards one another[115]. These three layers are firmly bound into packs, between which very weak attactive forces operate, which explains the low hardness, easy cleavage, and absence of elasticity in talc.

Talc is a poor conductor of heat and electricity. It does not melt below 1300–1400°C, and does not dissolve in acids even on heating[116]. Talc is widely used in the manufacture of rubber (as a filler), in perfumery, in the paint and ceramic industries (insulators, etc.), and in other fields[117].

A layer structure is possessed also by crystals of chrysotile asbestos, which forms fine fibres[118] sometimes reaching 160 mm in length. It is stable to the action of fire and alkali, but is broken down by hydrochloric acid. This material is of great practical value as a consequence of its stability at high temperatures.

The chief component of most clays is the mineral kaolinite $Al_4(Si_4O_{10})(OH)_8$, which is a variety of aluminium hydrosilicate. The crystals of kaolinite form two-layer packs, comprising a layer of silicon–oxygen tetrahedra and a "hydrargillite" layer. The structure of kaolinite crystals can be written

$$\begin{matrix} 6\,O \\ 4\,Si \\ 4\,O+2\,(OH) \\ 4\,Al \\ 6\,(OH) \end{matrix}.$$

They are easily cleaved into thin plates. The mineral is stable towards hydrochloric and nitric acids, but is readily decomposed by sulphuric acid, especially on heating. Kaolin is used in the ceramic industry (for the manufacture of china and pottery, firebricks, etc.), in building, and in other fields[119].

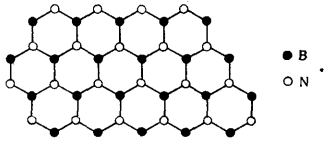
A layer structure is possessed also by montmorillonite. In contrast to kaolinite, it forms a three-layer structure comprising two layers of silicon–oxygen tetrahedra, between which is located a "hydrargillite" layer[120].

Micas are aluminosilicates which occur quite widely in Nature. Their composition can be expressed by the formulae[121] $M^+M_3^{2+}(AlSi_3O_{10})(OH)_2$ or $M^+M_2^{3+}(AlSi_3O_{10})(OH)_2$, where M^+, M^{2+}, and M^{3+} are uni-, bi-, and ter-valent cations. The hydroxyls may be replaced by fluorine. Micas are minerals having a crystal lattice of typical layered structure, in which 25% of the silicon–oxygen tetrahedra have been replaced by aluminium–oxygen tetrahedra.

A typical representative of the micas is muscovite $KAl_2(AlSiO_{10})(OH)_2$. As with many micas, the crystalline leaflets of this mineral are elastic on flexure[122]. It is stable towards acids. Muscovite possesses excellent electrically insulating properties, and is widely used for the manufacture of electrically insulating materials.

The manufacture of synthetic mica has now been organised[123–127]. It is produced in electric furnaces, by fusing together at 1370°C a stoichiometric mixture of magnesium oxide, aluminium oxide, silicon dioxide, potassium fluorosilicate, and orthoclase, and then slowly cooling the molten mass. The resulting mica has the same structure as the natural variety, but contains fluoride instead of hydroxyl groups, which confers on it a higher thermal stability (800°C) than natural mica (500–600°C).

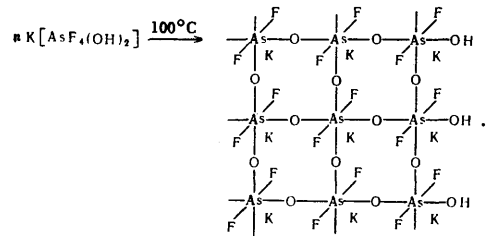
A layer structure resembling graphite is exhibited also by a variety of boron nitride BN:[128–130]



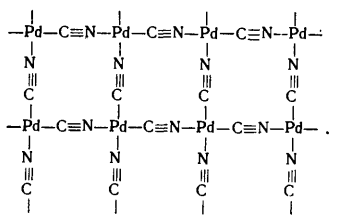
The distance between nitrogen and boron atoms is 1.45 Å, while that between the layers is 3.35 Å, as in graphite. Boron nitride can be prepared by heating boron and nitrogen above 1200°C or by heating boron or boron sesquioxide in an atmosphere of ammonia[131]. Boron nitride is a powder similar to talc, melting at ~ 3000°C (under pressure). It is stable towards acids and alkalis.

Crystals of the mineral molybdenite MoS_2 have a hexagonal structure of layer type[132,133], in which the molybdenum atom is surrounded by six sulphur atoms forming a trigonal prism. The unit cell of the crystal contains three lattices of molbdenum atoms, two layers of sulphur atoms being arranged between two of these lattices. Like graphite, molybdenum disulphide is easily cleaved, and is therefore used as a lubricant[134]. When rapidly heated in an inert atmosphere, it melts with decomposition at 1700–1800°C. At atmospheric pressure thermal dissociation of the polymer begins above 1300°C. In air molybdenum disulphide is stable up to 300–350°C; it is practically insoluble in water and dilute sulphuric and hydrochloric acids, but it dissolves in aqua regia and hot concentrated nitric and sulphuric acids[133].

Polymers of parquet type can be obtained by heating fluoroarsenates[135]:



According to Pauling[136] complex palladium cyanides have the structure



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PRODUCTION OF ORGANIC SURFACE FILMS BY THE ACTION OF ELECTRONS, ULTRAVIOLET RADIATION, AND THE GLOW DISCHARGE

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I. INTRODUCTION

The production of polymeric products on solid surfaces, by the action of electron bombardment or ultraviolet radiation on organic compounds of low molecular weight, or in the glow discharge, is of interest both from the theoretical point of view and in connection with the practical utilisation of this effect. Under these conditions films can be obtained from practically any organic compound, whereas with ordinary methods of polymerisation or polycondensation the presence of unsaturated bonds, rings, or certain functional groups in the molecules is essential. It is an extremely complicated task to establish the mechanism of the chemical reactions caused by the action of active particles on an adsorbed layer and leading to the formation of polymer films on the surface. It must be borne in mind that the resulting polymer is also subject to the action of ions and electrons, which may produce free macroradicals and cause degradation and cross-linking reactions. In view of the complexity and diversity of the reactions occurring under these conditions and leading to the formation of polymer films, only qualitative assessments can at present be made of their mechanism.

The method under discussion has already found practical application for the production of insulating and anticorrosive coatings. The thin polymeric films obtained in this way on a solid surface are distinguished by high thermal stability, chemical stability towards acids, alkalis, and organic solvents, good adhesion, and also homogeneity and the absence of pores. These properties of films, their superior dielectric characteristics, and the possibility of obtaining films of semiconductor type under special conditions indicate the wide opportunities for applying the method in various technical fields, and especially in microelectronics.

The present review will examine successively the possibilities and conditions for obtaining polymer films on solid surfaces by electron bombardment, in the flow discharge, and under the influence of ultraviolet radiation. Problems connected with possible practical uses of this method will be discussed separately.

II. PRODUCTION OF POLYMER FILMS ON IRRADIATION OF A SOLID SURFACE WITH ELECTRONS

Formation of polymeric films on solid surfaces under the influence of electrons occurs even with low concentrations of the organic substance in the gas phase, corresponding to pressures of 10^{-4} mmHg or lower. Consequently the processes governing film growth take place mainly in an adsorbed layer, since the probability of interaction between electrons and molecules in the gas phase is extremely small at such low pressures. Interaction between electrons and sorbed molecules may lead to a diminution in the concentration of molecules in the adsorbed layer or to the formation of polymeric deposits on sites which have been subjected to electron bombardment.

The qualitative view held at present on the mechanism of these processes is that desorption of molecules into the gas phase can take place only by inelastic collisions of electrons with the molecules: otherwise, the transfer of kinetic energy is too small to detach the molecules from the surface. In inelastic collisions, electronic states in the sorbed molecules can be excited, which may lead to dissociation of the molecules into fragments (ions and radicals). The fragments, which possess sufficient kinetic energy to overcome the bonding to the surface, are desorbed. Those fragments which have not acquired sufficient kinetic energy on dissociation remain on the surface, and may react either with one another or with molecules of the starting material, which will lead to the formation of solid polymeric deposits on the surface. Hence it follows that the interaction of electrons with sorbed organic molecules may lead simultaneously to the desorption of particles into the gas phase and to the formation of polymeric deposits on the surface. Henceforward we shall examine only one aspect of this process—the deposition of polymer films.

It must be mentioned, however, that very intensive research is now being undertaken into processes of the desorption of molecules under the influence of electrons. This is of definite interest for an understanding of the processes occurring in heterogeneous catalysis, and for radiation-chemical reactions on a solid surface. The investigations have shown (1) that the probability of desorption of molecules under the action of electrons is small[1]—from 10^{-3} to 10^{-5}—while the desorption of positive ions is still less probable[2], whereas the probability that molecules will be desorbed by ions approaches unity[3]. (2) The appearance potentials of ions from adsorbed molecules are lower than those of the same ions from molecules in the gas phase. This suggests that adsorption considerably changes the energy state of the adsorbed molecules in comparison with their state in the gas phase[1,4]. (3) Curves for desorption plotted against the energy of the electrons pass through maxima, whose positions agree well in most cases with the excitation functions of the molecules in the gas phase[5]. These results confirm that desorption is caused by dissociation of excited molecules and ions into neutral and charged species. (4) With electrons of low energy ($E < 6$ eV) the desorbed molecules do not differ in character from the initial molecules, which probably indicates that in this case

desorption is due to simple dissociation of complexes formed by the sorbed molecules with atoms of the support[6].

It is possible[7-9] to prepare graft polymer layers on various inorganic surfaces by exposing the latter to fast electrons (700 kV and more) in the presence of gaseous monomers. However, the conditions under which polymerisation takes place in this case (highly penetrating radiation, high vapour pressure of the monomer) are fundamentally different from those adopted in work on the action of electron bombardment, and therefore these results will not be discussed here.

1. Influence of Various Factors on Rate of Formation of Polymer Films by Electron Bombardment

The deposition of polymeric coatings on surfaces exposed to electrons in a vacuum was discovered as long ago as the 1930s. Stewart[10] observed the formation of insulating deposits when metallic substrates were bombarded with electron and ion beams. The electrical resistance of the films was measured as well as the breakdown voltage, and the films were also shown to be thermostable up to 450°C.

Further development of work on these lines resulted mainly from observations made when various specimens were examined in the electron microscope. It was found that, under the conditions of exposure in such an instrument, the specimens in time became covered with a brown coating and changed in size. This phenomenon was noted by many workers[11-14]. König and Winkler[15,16] observed the formation of carbon when specimens of organic origin were examined in the electron microscope. Cosslett[17] observed the formation of polymeric deposits on specimens of the oxides of nickel, molybdenum, and magnesium.

One of the first to make a special investigation of this phenomenon was Watson[18], who measured the size of carbon black particles in an electron microscope. He discovered that the particles increase in size with time owing to the formation on them of a light brown film. He suggested that the film resulted from the action of the electron beam on the vapours of organic substances.

Hillier[19] investigated the chemical properties of the film and the kinetics of its growth as a function of various factors. He showed that the film was insoluble in the usual organic solvents, strong acids, and alkalis, has an amorphous structure, and always contained carbon. The rate of film growth was proportional to the first power of the intensity of irradiation, did not depend on the material of the substrate, and fell with time. If, however, irradiation was terminated after a certain time, and was then begun again, the rate of growth reached its original value. This was explained[19] by a low rate at which the surface layer was filled with molecules. Hillier concluded that film formation occurs only when three factors—a vapour capable of yielding a polymer, a surface on which it can be formed, and a beam of electrons—are present. It was assumed that the surface was activated by the irradiation, and behaved as a catalyst. The organic molecules could reach the gas phase in two possible ways—by spontaneous diffusion from metal gaskets, the walls, and grease, and by degassing of metal parts of the instrument under the influence of electron bombardment. To prevent film formation this author recommends first eliminating the access of organic substances to the gas phase.

Ennos[20] used a specially designed apparatus to investigate the cause of the deposition of films on solid surfaces and methods for their elimination. Direct measurements of film thickness established that the films grow at a rate of 1 Å s^{-1} with a current density of 0.5 mA cm^{-2}, electrons of energy 40–75 keV, and a pressure of 10^{-5} mmHg. He showed[20] that the rate of growth of the film is independent of the duration of exposure or the energy of the electrons within the above range, although it is strongly dependent on the temperature of the substrate. Discussing the mechanism of film formation, this author concluded that the deposits were formed by the interaction of organic molecules with the electron beam on the surface of the substrate, where a considerable concentration of hydrocarbon molecules is produced by adsorption. This same view on the mechanism of the formation of polymeric deposits was held also by Poole[21], who emphasised that, even with the organic substances at pressures of 10^{-4} mmHg and above, all processes responsible for film formation take place on the surface, not in the gas phase.

Several suggestions had been made even earlier to explain this phenomenon. Watson[18] assumed that film formation was due to ions produced in the residual atmosphere and deposited on the support near the electrically conducting surface. However, an estimate of the deposition due to ions formed in residual gases gives values for the reaction velocity which are smaller by several powers of ten than those observed experimentally.

Cosslett[17] supposed that film formation was due to ejection of adsorbed substance, perhaps of metal itself from the grid of the specimen-holder, on electron bombardment.

Haefer[22] noted that deposition of a substance on a substrate may result not only from the reactions of electrons and ions with adsorbed molecules but also from cathode sputtering. Ellis[23], like most workers, considered that a film was formed as a result of resinification of organic substances under the influence of the electron beam, but differed in ascribing replenishment of the number of adsorbed molecules mainly to the migration of molecules on the surface, while replenishment from the gas phase was of considerably less importance. However, Ennos[20], on the basis of the experimental results, reached the opposite conclusion—that replenishment of the number of adsorbed molecules by surface migration played an insignificant part in comparison with that from the gas phase.

Thus study of the reasons for contamination of specimens in an electron microscope and elucidation of the conditions under which it would be minimised have led to establishment of the important fact that the formation of polymeric deposits results from interaction of electrons with molecules in the surface layer.

In later work, where experiments have been made both in specially designed apparatus and in electron microscopes, the kinetics of film formation and the factors influencing the rate of growth have been studied quantitatively and in greater detail. The experimental techniques have been described in detail in the original papers, so that they will merely be mentioned here. Film thickness has been determined interferometrically[24,25], by means of a piezoelectric crystal[26], and by weighing[27]. Films of a sputtered metal[28,29] and of a dielectric[25] (quartz, glass) were employed as substrates. Experiments were made mainly in an atmosphere of the vapours of certain organic substances, but in some work use was made of an atmosphere of the residual gases in vacuum equipment, which always contain hydrocarbons.

The relative abilities of various organic substances to contaminate vacuum equipment was studied[30] by introducing them into a clean vacuum system, and then determining the characteristics of the polymeric deposits formed on surfaces bombarded by electrons. The tendency to film formation diminished in the sequence—hydrocarbon oil of diffusion pumps, vacuum greases, various types of rubber gaskets, silicone oil, and vacuum wax. Experiments carried out at the same time on the temperature dependence of the rate of deposition showed that raising the temperature to 200°C reduced the rate of film growth to 10% of its previous value. A cold trap at −15°C has a similar effect.

The influence of the temperature of the substrate on the rate of film formation on the surface has been investigated for various organic compounds[20,24,26,30-34]. Leisegang and Schott[32] studied the effect of temperature on the rate of contamination of a specimen in an electron microscope, and found the rate to diminish with rise in temperature. Christy[25] studied the rate of formation of films from the silicone oil DS 704 as a function of the current density of electrons with the substrate at various temperatures, and confirmed that rise in temperature diminishes the rate of film growth. Haller and White[26] studied the dependence of the rate of polymerisation of butadiene on its pressure in the gas phase (over the range 10^{-6}–3×10^{-4} mmHg), and established that the rate diminishes with rise in temperature throughout the pressure range investigated.

Several investigations have been made of the influence of the nature of the substrate on the rate of formation of polymeric deposits[19,21,35]. Experiments with silver, steel, copper, nickel, and copper–nickel alloy substrates revealed no dependence of rate of film growth on substrate material[21]. This is confirmed by the results of other work[19]. A study of film formation on nickel, copper, platinum, silver, iron, glass, and crystalline sodium chloride substrates in an electron microscope[35] yielded no definite conclusions on the influence of the substrate on the rate of film formation. The fact that no such relationship was observed in the above work is probably due to a phenomenon subsequently discovered by Mann[36], who studied the secondary electron emission from polymeric films under the influence of an electron beam. He found that, up to a film thickness of 25 Å, secondary emission occurs simultaneously from the growing film and from the substrate, whereas with thicker films secondary emission is observed only from the growing films themselves. It was shown that, with the substrate at a positive potential relative to the electrode accelerating the electron beam (which is usually the case in all experiments), secondary electrons also play a definite part in film formation. It may be concluded from this work that the material of the substrate can influence the rate of film growth only in the early stages of the process.

The influence of the vapour pressure of organic substances has been investigated[25-27,37]. Haller and White[26] determined the dependence of the rate of film growth on the pressure of butadiene over the range 1.3×10^{-6}–3.2×10^{-4} mmHg, and found the rate to increase with rise in pressure only to a certain limit, this saturation occurring at higher pressures with greater electron currents (Fig. 1). Similar pressure effects have been observed[27] in an investigation of the behaviour of silicone oil, and also in other work[19,25]. In another piece of work[37] the rate of film growth was found to be independent of the pressure of butadiene. This was probably because these experiments were conducted at high pressures, at which the rate had ceased to depend on pressure.

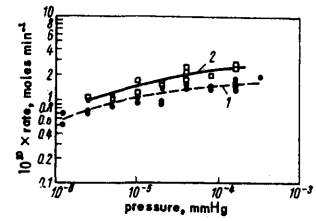


Fig. 1. Pressure dependence of rate of polymerisation of butadiene at: 1) 400 μA; 2) 800 μA.

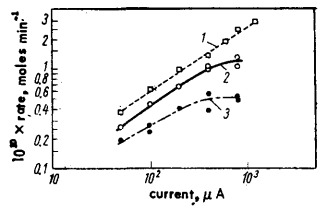


Fig. 2. Dependence of rate of polymerisation of butadiene on the current at pressures of (mmHg): 1) 1.6×10^{-4}; 2) 4.0×10^{-5}; 3) 1.3×10^{-5}.

The influence of the current density of the electron beam on the rate of film formation has been investigated[19,24-26,32]. Christy[24] found that, with a silicone oil, the relation is non-linear, the rate reaching saturation at definite values of the current. Haller and White[26] showed the rate of film formation from butadiene to be proportional to the square root of the current density. At higher currents the curves tend to form a plateau, this occurring at higher current densities the higher the pressure (Fig. 2). Similar results for the influence of current density on rate of film formation were obtained by other workers[32], and also more recently[38,39].

No detailed study has yet been made of the dependence of the rate of film growth on the electron energy. Only isolated experiments have been made, and in these the relationship was investigated only over a narrow energy range. Thus the rate at constant current density and pressure has been found[20] not to depend on the energy of the electrons over the range 40–75 keV. Nor does variation over the range 200–600 eV influence the rate of film formation from silicone oil[27]. Mayer[38] made experiments in a reflecting electron microscope, and found the rate to increase with low electron energies over the range 6–25 eV.

The influence of the duration of irradiation on the rate of formation of films has been examined[20,24,26,27,38]. Over the times investigated the rate was found to be independent of duration. A constant rate of growth is maintained[24,27] for film thicknesses of several thousand Ångström units.

It has been shown[24,40] that films of either semiconductor or metallic type can be obtained by irradiating solid surfaces with electrons in an atmosphere of the vapour of an organometallic compound [or of an inorganic salt of the tin(II) chloride type]. Baker and Morris[40] have demonstrated that, under more severe experimental conditions

(electrons of energy up to 1 keV, current density of ~ 5 mA cm^{-2}), the decomposition of the vapours of organometallic compounds (tetrabutyltin, tetramethyltin, tetraethyl-lead) proceeds as far as formation of a film of the pure metal on the surface of the substrate. Decomposition of tetrabutyltin $(C_4H_9)_4Sn$ on a quartz surface yields [25] films not of pure tin but of polybutyltin, possessing semiconductor properties. Both the rate of growth and the composition of the films depend on the pressure of tetrabutyltin vapour in the gas phase, the current density, and the temperature of the substrate. The same work included an examination of the formation of tin films by the decomposition of tin(II) chloride molecules by electrons on a quartz substrate.

2. Mechanism of Formation of Polymer Films

Most research workers consider that film formation is due to processes occurring in the surface layer as a result of interaction between sorbed molecules and electrons. The mechanism of film formation has been discussed in greater detail [24,26,37,41]. The process is supposed to occur in two stages: (1) active centres (radicals and ions) are formed on the surface by interaction of electrons with sorbed molecules; and (2) sorbed molecules react with these active centres. The surface formation of polybutadiene films, in particular, has been interpreted in this way [26,37,41]. These authors consider that the polymerisation of butadiene proceeds initially on the surface of the substrate, and continues as the film grows by interaction of adsorbed gas molecules with active centres of the polymer surface.

There is no generally accepted view in the literature as to whether ions or radicals play the main part in the process. Several workers assume a radical mechanism. This conclusion was reached by Christy [24], who examined the behaviour of silicone oil, and found that polymer formation results from the recombination of free radicals produced by the action of electrons on adsorbed molecules. Haller and White [26] supply evidence that the surface polymerisation of butadiene proceeds by an ionic mechanism. It is most likely that both mechanisms of polymerisation may play a part in film formation, with one or the other predominating depending on the experimental conditions and the nature of the molecules of the starting material. Schemes have been discussed [26] for both mechanisms applied to the polymerisation of butadiene on the surface of an already formed film.

The radical mechanism of polymerisation can be represented by the equations

$$P + e \rightarrow P^{\cdot} + H^{\cdot} + e \quad k_1 I \tag{1}$$

$$P^{\cdot}_M + Bu_a \rightarrow P^{\cdot}_{M+1} \quad k_2 [P^{\cdot}]\ [Bu_a] \tag{2}$$

$$P^{\cdot}_M + P^{\cdot}_N \rightarrow P_{M+N} \quad k_3 [P^{\cdot}]^2 \tag{3}$$

where P is a polymer molecule, Bu_a is an adsorbed butadiene molecule, P_M and P_N are polymer molecules on the surface containing respectively M and N monomer units, and k_1, k_2, and k_3 are the rate constants of reactions (1)–(3) respectively. On the assumption that the size of a radical does not affect its chemical properties and that the concentration of adsorbed monomer is constant, the rate of polymerisation can be written

$$r = -\frac{d[Bu_a]}{dt} = k_2 \sqrt{\frac{k_1}{k_3}} I [Bu_a]. \tag{A}$$

The relation between the pressure of butadiene in the gas phase and the surface concentration of its molecules $[Bu_a]$ is determined by the adsorption isotherm.

The ionic mechanism of polymerisation is described by the equations [26]

$$P + e \rightarrow P^{+} + H^{\cdot} + 2e \quad k_4 I \tag{4}$$

$$P^{+}_M + Bu_a \rightarrow P^{+}_{M+1} \quad k_5 [P^{+}] [Bu_a] \tag{5}$$

$$P^{+} + e \rightarrow P \quad k_6 [P^{+}] I \tag{6}$$

$$P^{+} + e_c \rightarrow P \quad k_7 [P^{+}] [e_c] \tag{7}$$

$$e_c + s \rightarrow e_s \quad k_8 [e_c] \frac{dv}{dx} \tag{8}$$

$$e_c + L \rightleftarrows e_L \quad [e_c] = [e_L] \exp(-E_L/kT) \tag{9}$$

where P is a polymer molecule, P^{+} a polymer molecule with a positive charge localised on one of the surface carbon atoms, e an incident electron, e_C an electron in the conduction band, e_L an electron in a trap of energy level L lying below the conduction band of energy E, and k_4–k_8 are the rate constants of the corresponding reactions. Equation (8) implies the transfer of a conduction electron into the metallic substrate s under the influence of the potential gradient dv/dx. If we consider that stage (8) is rapid, i.e. that there will be no great accumulation of charge in the polymer, we have

$$[P^{+}] = [e_c] + [e_L] \simeq [e_L]. \tag{10}$$

On the assumption that concentrations are constant, and that stage (7) is much more rapid than stage (6), the rate of polymerisation can be expressed in the form

$$r = k_5 \sqrt{\frac{k_4 I}{k_7 \exp(-E_L/kT)}} [Bu_a]. \tag{11}$$

In the deduction of this equation and of Eqn. (A), reactions such as the formation of cross-links and unsaturated bonds, etc. have been disregarded, since they do not affect the rate of polymerisation.

It is seen from Eqns. (A) and (11) that in both cases the rate of polymerisation is proportional to the concentration of sorbed butadiene molecules and to the square root of the electron current: i.e. the type of dependence of r on $[Bu_a]$ and I provides no opportunity of assessing the mechanism of polymerisation. Hence it follows that additional data are necessary in order to elucidate the mechanism of polymerisation.

Experimental results are now available which indicate unambiguously that in several cases the radical mechanism of polymerisation may play a considerable part. Mayer [38] has shown that films can be obtained with electrons of energy below 6 eV, i.e. under conditions such that ions cannot be formed. This mechanism of polymerisation is supported also by the fact that the resulting films contain considerable concentrations of free radicals [28,29] (up to 10^{18} spins cm^{-3}). Christy [24] has given a theoretical expression for the rate of formation of films by a radical mechanism, which shows good agreement with his experimental data obtained with the vapour of silicone oil. Other authors [20,21,27] consider that in the cases which they have investigated films are formed also predominantly by a radical mechanism.

On the other hand, Haller and White [26], in a paper on the polymerisation of butadiene on a surface, give experimental data supporting an ionic mechanism. To determine the mechanism of polymerisation they used mixtures of butadiene with oxygen (4 : 1) and with hydrogen (1 : 4). If a

radical mechanism of polymerisation is assumed, the presence of oxygen should result either in complete suppression or to a slowing down of polymerisation; hydrogen should have a similar effect, and its presence should lead to an increase in the rate of migration of free radicals in the polymer and an increase in k_3 in Eqn. (3). It was found, however, that, within the limits of experimental error, the rates of polymerisation of pure butadiene and of its mixtures were the same when the partial pressures of butadiene in the mixtures were equal to its pressure in the experiments on the polymerisation of the pure monomer. This was regarded as indicating that butadiene polymerises by an ionic mechanism. This view is supported also by the fact that the life of positive ions in the polymer, determined [26,27] by means of a pulsed electron beam, is very long (around 1–3 min).

The preceding arguments have applied to the polymerisation of organic molecules on the surface of already formed polymer. However, formation of the first layer of polymer film directly on the pure metal surface has been found to involve far more rapid polymerisation than in the formation of subsequent layers. Hirsch [42], comparing his experimental results on the production of polymer films of monolayer thickness with those obtained by Ennos [20] on the formation of films several thousand Ångström units thick under roughly similar conditions, found that the rate of film growth was higher in the former case by factors of the order of 10^2. White [39] established that one incident electron causes the polymerisation of 30 butadiene molecules in the case of a pure metal surface, whereas on a previously formed film the polymerisation of one butadiene molecule requires 100 electrons. Such a difference in the rates of formation of the first layer of a film compared with that of subsequent layers is explained by the author in terms of the energy state of molecules adsorbed on the clean metal surface being such that only slight action by electrons is required for the chain reaction of polymerisation to begin. It must also be borne in mind that a high rate of formation of the initial layers of a film may be considerably affected also by secondary electrons dislodged from the substrate metal [36].

3. Structure and Properties of Films

Little work has been done on the structure of polymer films obtained on a surface by electron bombardment. This method probably does not allow films of ordered structure to be produced [38]. X-Ray examination has shown the films to be amorphous [19,33,43-45]. Infrared spectroscopy has been used in several cases to investigate the structure of the films. The infrared spectra [27] of films obtained, in an atmosphere of a silicone oil, on the surfaces of stainless steel and of an optically polished sodium chloride crystal contained in both cases a broad absorption band in the region of 1050 cm^{-1}, corresponding to stretching vibrations of the Si–O–Si group, together with absorption bands corresponding to vibrations of the $Si–CH_3$ bond, deformation vibrations of the Si–O bond, and oscillations of a hydrogen atom in CH_2 and CH_3 groups. The absorption spectrum of the film obtained on the metallic substrate also included a band in the region of 1750 cm^{-1}, indicating the presence of carbonyl groups in the film, and a broad band near 3400 cm^{-1}, corresponding to the hydroxy-group. The appearance of carbonyl and hydroxyl groups in the film is probably due to oxidising processes, as in the irradiation of ordinary polymer films with electrons [46,47]. The

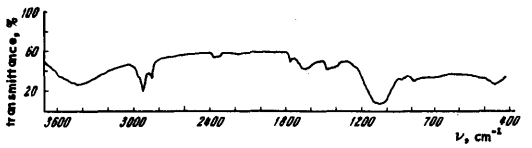
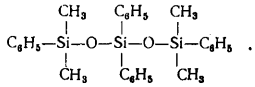


Fig. 3. Infrared spectrum of film obtained from silicone oil.

absorption band in the region of 1620 cm^{-1} for the film obtained on sodium chloride, and 1645 cm^{-1} for the film obtained on the metal, is especially interesting, for it indicates the presence of double bonds in the films. The infrared spectrum of the polymer film obtained on a stainless steel substrate is reproduced in Fig. 3.

The possible structure of films obtained from the silicone oil DS 704 is discussed by Holland and Laurenson [34]. The chemical formula of the oil (M = 484) is



The action of a discharge and of γ-rays on this compound in the gas phase gave large quantities of hydrogen and methane with little benzene. From this it is concluded that the phenyl group remains in the polymer molecule, the monomer units being linked by CH_2 and $CH_2.CH_2$ groups.

Several workers have examined the physical and chemical properties of the films [19,24,42-44]. Films obtained from organic compounds always contain carbon and hydrogen [19], sometimes also oxygen [11], and can be removed from the surface by heating in air to redness [10,19]. The films are insoluble in water, the usual organic solvents, and also strong acids and alkalis. They possess high thermal stability [10,43,44], especially those obtained from silicone oils [43]. The present method also enables especially thin films to be obtained, possessing good homogeneity [37], continuity [24,42], adhesion to the substrate surface [27,44], and superior dielectric properties [24,27].

Many studies have been made [10,24,27-29,34] of the electrical properties of films obtained in atmospheres of organic and silicone compounds. The film possess high values of the bulk resistivity R_v and the breakdown voltage [24,27]. Table 1 gives estimated values of R_v, the dielectric constant ϵ, the tangent of the loss angle tan δ, and the breakdown voltage v_{br} for films from silicone oil [27].

The electrical conductivity of the films varies between wide limits depending on the energy of the electrons, the temperature, and the material of the substrate. Poole [21] showed that films having a high resistance are obtained with electrons of energy below 300 eV, whereas films of low resistance are obtained above this value. Zinn [33] has investigated the influence of the substrate material on the insulating properties of the films: films obtained on

TABLE 1.

R_v, ohm cm	ϵ	tan δ	v_{br}, V cm^{-1}
$1 \cdot 10^{-14}$	3—4	<0.01	$>10^6$

aluminium and tin possess good insulation, those on lead have moderate insulation, and those on gold and silver possess no insulating properties. He suggests[33] that the good properties on aluminium and tin are due to thin oxide films at the metal–dielectric interface. Experiments on the influence of the substrate temperature on the electrical conductivity of the film show[34] that those obtained at 240°C have a resistance of 6.5×10^9 ohms cm^{-2}, while those produced at room temperature have a value of 10^{13} ohms cm^{-2}. Nevertheless, films obtained at +50°C and −196°C have identical insulating properties. The absence of variation in electrical conductivity with temperature over this range is attributed[34] to similar coefficients of adhesion of the silicone oil molecules at these temperatures.

Holland and Laurenson[34] have investigated the effect, on the dielectric properties of films obtained from silicone oil, of adding various gases (oxygen, nitrogen, hydrogen, carbon dioxide, and water vapour) during their preparation. It was found that addition of oxygen and water vapour to the silicone oil vapour resulted in films showing higher resistance in air than in a vacuum, whereas films obtained with additions of nitrogen, hydrogen, and carbon dioxide show a higher resistance in a vacuum. The latter result was explained by adsorption of water vapour on the surface of the film in air. The dielectric constant ϵ of the films was 2.3 and 4.0 with additions of carbon dioxide and hydrogen respectively.

A considerable growth of interest has recently occurred in the mechanism of the passage of current through thin insulating films, including polymer films; the main reason for this interest is the need to use them for controllable sources of current, such as cold-cathode emission devices and tunnel triodes. The principle on which such devices operate has been discussed[48]. Two main mechanisms by which electrons can be transmitted through thin insulating films—passage of current by the tunnel emission of electrons and by Schottky emission—have been considered in the literature, and can be distinguished by the dependence of current on voltage and temperature (Table 2). Transport of current by the tunnel effect is independent of temperature, and is observed in extremely thin films (~ 100 Å), where the mean free path of the electrons in the film is comparable with its thickness. Transport of current by the Schottky mechanism occurs with thicker films, and is strongly dependent on temperature.

Studies have been made of the mechanism by which current passes through thin polymer films and of their electrical properties[28,29,49]. Mann[28] has examined the electrical properties of films obtained in the vapour of the silicone oil DS 704. Measurements were made of the current in the M–P–M system, over the range of film thicknesses 500–2500 Å, as a function of voltage and temperature (the system comprised a polymer film P enclosed between two sputtered metal electrodes M). At voltages up to 5 V the current density varies exponentially with the electric field strength, and is independent of film thickness. When the voltage is increased above 5 V, the current decreases, to disappear completely at ~ 6 V. A typical curve showing the variation in current density I with voltage is shown in Fig. 4.

The electrical conductivity of the films is strongly dependent on temperature at high voltages, but at low voltages, in the region of the negative resistance effect, the conductivity is independent of temperature. Christy[29] has investigated the electrical properties of analogous films over the thickness range 50–150 Å, and found that at low voltages (< 1 V) the current increases linearly with voltage, whereas at higher voltages it obeys the law $\ln I \propto V^{1/2}$. An investigation[49] of the conductivity of a polymer film 100 Å thick showed that $\lg I \propto V^{1/2}$ for voltages from 0.04 to 1 V. The temperature dependence of current for this film is reproduced in Fig. 5. The departure of this curve from a straight line is explained by a mixed mechanism for the transmission of electrons: a current due to tunnel emission is superimposed on the current due to Schottky emission, and makes a particularly large contribution at low temperatures.

The effect of ageing the film in air on its electrical properties has been investigated[28,29]. The volt–ampere characteristics gradually move to the right as the films remain in the air, and at the same time the capacitance of

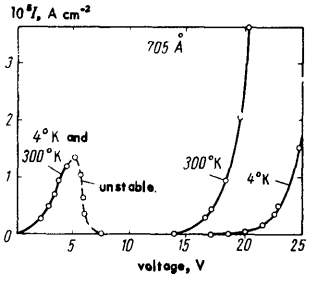


Fig. 4. Voltage dependence of current density in the M–P–M system.

TABLE 2. Dependence of current on voltage and temperature for two mechanisms of electron transfer.

Emission	Voltage dependence	Temperature dependence
Tunnel	$I \propto V$ for $I < \Phi$ $I \propto V^2 e^{-\text{const}/V}$ for high V	none
Schottky	$I = \alpha \exp(BV^{1/2})$	$I \propto T^2 e^{-\text{const}/T}$

Φ = work function between metal and polymer film; α and B are constants.

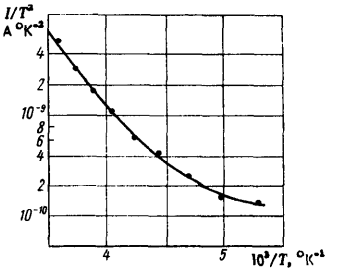


Fig. 5. Temperature dependence of current for a film obtained from the silicone oil DS 704.

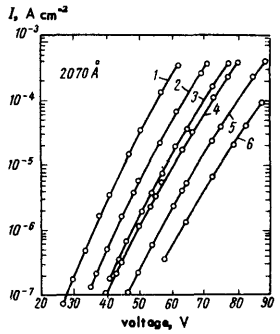


Fig.6. Dependence of current density on voltage for a film left in air over different periods.
1) 5 min; 2) 26 h; 3) 72 h; 4) 96 h; 5) 192 h; 6) 360 h.

the M–P–M system increases (Fig. 6). Placing the system in a desiccator resulted in a change in its electrical conductivity analogous to that occurring in the air, while the capacitance remained unchanged with time under these conditions. When, however, the system was placed in a vacuum or in an atmosphere of dry nitrogen, neither the conductivity nor the capacitance changed with time. It is concluded [28,29] that the change in conduction of the M–P–M system in air is associated with the adsorption and diffusion of oxygen molecules into the film through the electrodes, while the change in capacitance of the system is caused by the adsorption of water vapour. It has also been observed that the variation in the conductivity of films in air parallels the variation in the concentration of free radicals formed in the film during its preparation (the films contain high concentrations of free radicals, ~ 10^{18} spins cm^{-3}). This indicates that the mechanism of electrical conduction in the films is connected with free radicals, and that in this case the radicals are probably acting as electron-traps.

III. PRODUCTION OF POLYMER FILMS IN THE GLOW DISCHARGE

The chemical reactions leading to the formation of polymer films in the glow discharge are considerably more complicated and diverse than those occurring under the influence of a beam of electrons. This is due both to the high pressures and current densities (~ 1 mmHg and 0.1–1 mA cm^{-2}) and to the energy distribution of electrons in the discharge zone. A consequence of this distribution is that various electronic states in complicated organic molecules are already excited at the primary interaction step, so that a variety of dissociation fragments are formed. Furthermore, the breakdown of organic molecules may be caused by the action of free radicals and hydrogen atoms formed as a result of the primary reactions, since high pressures in the discharge zone favour the occurrence of secondary processes in the gas phase. It follows from this that the great diversity of chemical changes which organic molecules usually undergo under the influence of a glow discharge is not always due to the discharge itself, but is often a consequence of secondary processes caused by various neutral species. Hydrogen atoms can probably exert an especially large influence on chemical reactions in the discharge, since it has recently been established that they can possess high energies, close to the ionisation potential of the hydrogen atom, and the reaction cross-section for such excited particles far exceeds the usual gas-kinetic cross-section [50].

It follows from the above that film formation on a surface in a glow discharge may be caused not only by charged species, as occurs under the influence of electrons and ions, but also by active neutral species formed in the discharge zone, their concentration in the plasma far exceeding the concentration of charged species. It is also possible that ultraviolet radiation, produced by spontaneous loss of excitation by particles, may play some part in initiating the surface process.

As early as 1874 Thénard [51] and Wilde [52] noted that the action of an electric discharge on hydrocarbon vapours resulted in the formation of solid deposits on the walls of the apparatus. A later study (in the 1930s) of the chemical action of a glow discharge on methane showed [53] that, in a negative discharge at the temperature of liquid air, methane underwent dissociation followed by condensation. At room temperature dull yellow deposits were formed on the walls, which were unaffected by the usual solvents.

Austin and Black [54,55] studied the chemical behaviour of several cyclic hydrocarbons in a Tesla discharge. They found that a coating similar to shellac was formed on the walls of the reaction vessels, and solid reaction products condensed in a liquid nitrogen trap. With cyclohexane, benzene, toluene, and *p*-xylene the thin films resembling shellac were sometimes reddish brown or black in colour, and sometimes almost colourless. The freshly prepared films had good adhesion to the surface, but on standing they peeled off and cracked. The films did not dissolve in alcohol, acetone, ether, turpentine, benzene, toluene, xylene, or water, and were unaffected by the usual acids and alkalis. Elementary analysis of the films showed them to contain oxygen as well as carbon and hydrogen. From the results the formulae $(C_9H_7O_2)_x$, $(C_{21}H_{19}O_3)_x$, and $(C_{19}H_{19}O_3)_x$ were proposed for the solids present in the films formed from benzene, toluene, and xylene respectively.

Linder and Davis [56] investigated the behaviour of 57 different hydrocarbons in the discharge. In almost all cases they observed the formation of solid products on the cathode, the anode, and the walls of the discharge tube. These products were dark brown or black, mostly waxlike, but sometimes brittle. They evidently contained much carbon, although they did not burn completely on analysis.

Stewart [10], working with a discharge in a vacuum of around 10^{-5} mmHg, obtained insulating films which were insoluble in the usual solvents. He concluded that the films were of hydrocarbon origin, probably formed from residual gases and also from the vapour of the vacuum grease.

At the present time polymer films are obtained in a discharge usually under a vacuum bell jar at pressures of the order of 0.001–0.1 mmHg. [57-69] As an example let us consider the equipment for the production of thin polymer films patented by the [American] General Electric Co. [68] (Fig. 7). The pressure under the bell jar is ~ 0.02 mmHg, the electrodes are 16 mm apart, and the voltage between them is 1000 V. The optimum pressure range in the system is 0.01–0.1 mmHg. Polymer films less than 5 μm thick, possessing good dielectric characteristics, have

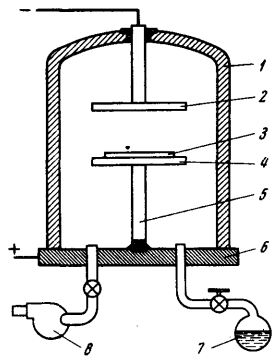


Fig. 7. Diagram of apparatus for the preparation of thin polymer films in a glow discharge:
1) vacuum bell jar; 2), 4) electrodes; 3) plate on which a film is sputtered; 5) electrically conducting support; 6) tile; 7) vessel containing initial monomer; 8) pump.

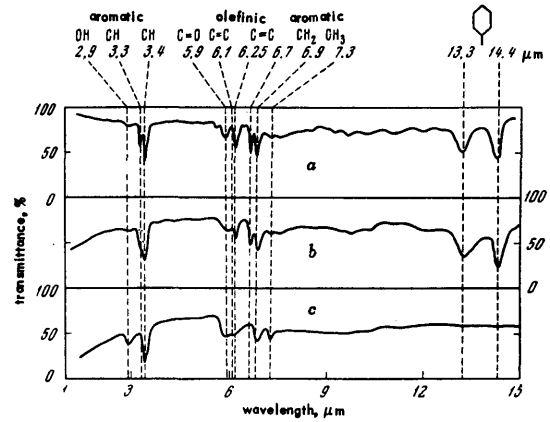


Fig. 8. Infrared spectra of polymer films obtained from benzene and methane:
a) polystyrene foil irradiated with electrons; *b*) polymer film obtained from benzene; *c*) polymer film obtained from methane.

been obtained by this technique. The substrates on which the films are deposited have usually been of synthetic rubber metallised with aluminium, but films can be deposited on other materials—glass to which a surface layer of metal has been applied, metallic and siliceous plates, etc.

Coleman[61] uses as substrates moving tapes, which are gradually removed from the discharge zone, to obtain films of constant thickness undamaged by the heat evolved in the process.

König and Helwig[70] and Brockes and König[71] studied polymer films obtained from benzene vapour. In the former case[70] the discharge current was 7–9 mA and the voltage ~ 1000 V. The elementary composition of the film was determined ($C_{1.00}H_{0.83}$), its mass (by weighing on a quartz balance), its thickness with a Zener interferometer, and its density. These films proved to be less dense than carbon or graphite. The electrical conductivity of the films was ~ 10^{-9} ohm^{-1} cm^{-1}. The properties of the films were considerably changed by vacuum heat-treatment above 100°C. The optical transmission of the films was substantially diminished, and at 400°C they became first brown and then black. Heating the films produced an especially marked change in their electrical conductivity, which had increased by factors of 10^{10} after heating to 600°C.

Infrared spectroscopy was used[71] to establish the structure of the films. The infrared spectra of films obtained from benzene contained absorption bands characteristic of aromatic groups, whereas these bands were absent from the spectra of films obtained from methane (Fig. 8). It is interesting that the infrared spectra of a polymer film obtained from benzene and of a polystyrene film which had been irradiated with electrons had much in common with respect to both the character and the intensity of the bands. On storage in air the films underwent oxidation, and the infrared spectra contained bands corresponding to C=O and O–H bonds. Similar bands were observed also after irradiation of the film with electrons. Infrared spectroscopy was used also to investigate the oxidation of films from benzene as a function of their storage time in air (Fig. 9).

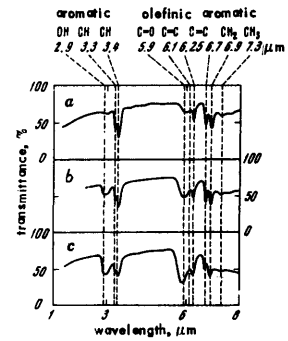


Fig. 9. Variation in infrared spectrum of polymer films obtained from benzene with time of storage in air:
a) 2 h; *b*) 5 days; *c*) 1 month.

If the films were heated in a vacuum immediately after preparation, they underwent no subsequent oxidation in air.

The influence of the conditions and parameters of the discharge on the properties of the resulting films was also investigated. An appreciable decrease in the hydrogen content of the films was observed, together with a diminished rate of film growth, when the discharge voltage was increased to 3000 V. Increase in the voltage also produced an increase in the quantity of degradation products of low molecular weight and the number of conjugated double bonds formed.

Pagnia[62,72] showed that the properties of films obtained in benzene vapour in a glow discharge depend to a considerable extent on the conditions of the discharge. With the same ignition voltage the films differ in electrical conductivity depending on whether the substrate is cooler or heated: it has the values 0.1 and 100 ohm^{-1} cm^{-1} respectively. Pagnia put forward the hypothesis that, with high ignition voltages and "hot" substrates, the films consist of

carbon alone, which may explain their relatively high conductance and great stability. This hypothesis was confirmed by the infrared spectra: the carbon content of films obtained with a "hot" substrate was very high, while the hydrogen content was insignificant. Nevertheless, the vacuum annealing of films obtained at low ignition voltages leads to a considerable loss in weight. The dependence of the resistivity on the ignition voltage, taking into account the temperature of the substrate, is illustrated in Fig. 10. Pagnia showed also that the resistance of the films remains constant on storage in a vacuum, but increases on storage in air, reaching a constant value only after several days (Fig. 11). Furthermore, all types of films obtained showed an increase in conductance with temperature.

Vastola and Wightman[73] also studied the behaviour of several hydrocarbons—ethane, methane, and ethylene (Group A) and acetylene, benzene, and naphthalene (Group B)—in a high-frequency discharge. The main product with both groups of hydrocarbons was a film a few Ångström units thick having a definite H/C ratio, and almost all the films absorbed a further quantity of hydrogen from the discharge, the ratio reaching a limiting value of 1.6. The films were insoluble in organic solvents. They were shown to be amorphous by X-ray and electron diffraction. The infrared spectra showed films of Group B to possess greater unsaturation than those of Group A, and the latter contained no aromatic groups. A high concentration of free radicals was found in films of Group B. According to the authors these results were consistent only with a mechanism of film formation which was independent of the type of bond in the initial hydrocarbon.

The electrical properties of films obtained in the glow discharge from 40 different substances have been investigated by Bradley and Hammes[57,74] and by Bradley[75]. The films were prepared at a pressure of ~ 1 mmHg, a current density of 1–3 mA cm^{-2}, and a voltage of 300–400 V, the thickness of the films being controlled by the discharge current and the time. These authors assume that the

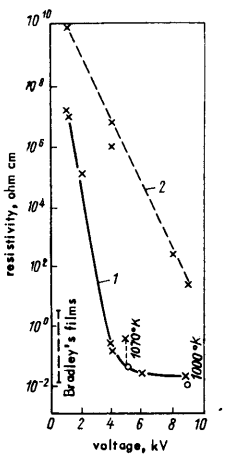


Fig. 10. Dependence of resistivity of film on ignition voltage of discharge with the temperature of the substrate taken into account:
1) substrate heated at 675° ± 15°K;
2) substrate cooled.

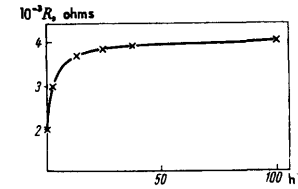


Fig. 11. Variation in resistance of film with duration of exposure to the air.

mechanism of conduction in the films studied in the same to a first approximation, although differences are observed in the structure, appearance, and stability of the films. The absorption of oxygen has no fundamental effect on the conductance (which is approximately doubled on the absorption of ~ 10 wt.% of oxygen). It was suggested that the magnitude and temperature dependence of the conductance are explained by the predominance of C–C bonds in the film structure. The same workers[74] investigated the photoconduction of films obtained in the glow discharge and containing nitrogen, sulphur, selenium, and several metals. They showed that the photoconductance varies by several orders of magnitude depending on the composition of the films, and a considerable increase in the photocurrent is observed with rise in temperature from −77°C to 185°C. The principal factor associated with photoconduction is probably the concentration of unsaturated groups in the films.

Bradley[75] has investigated the dark conductance and the photoconductance of polymer films obtained in a discharge, as functions of the temperature and the voltage during measurement. With most of the specimens examined the current was proportional to the voltage raised to a power exceeding unity: $I \propto V^{\Delta}$ ($\Delta > 1$). With many specimens the exponent Δ remains constant over a wide range of temperatures, although some highly conducting films show a sharp increase on heating above 180°C, after which Δ remains unchanged on cooling to room temperature. Films obtained from several sulphur, selenium, and nitrogen compounds gave values of the exponent Δ = 1–1.3, with the exception of films prepared from malononitrile. Such films and also those obtained from ferrocene exhibit a considerable increase in Δ on heating to 180°C. The activation energy of conduction was also determined, and for most of the films proved to be 0.4 ± 0.1 eV. It drops appreciably below 0°C, and may reach 0.1–0.2 eV. The author remarks that no theory is yet available to explain the temperature variation of Δ and of the activation energy.

Several papers have discussed a suggested mechanism for film formation in the glow discharge[57,60,76–78]. Goodman[60] assumes that ionised species form a polymeric substance on the electrode surfaces. Since the resulting polymer is again bombarded by ions, the same consequences—degradation and cross-linking—can be expected as with high-energy irradiation. Bradley and Hammes[57] proposed a mechanism consisting in the formation of ionic and radical-ion fragments by the intense electron bombardment, with recombination of these fragments on the electrodes. Haefer[76,77] assumes that molecules are ionised in the gas space of the glow discharge, forming intermediate products—free radical-ions—which exhibit a great tendency to recombine, and on striking the electrode surfaces form solid polymers.

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Thus investigators have reached essentially the same view of the possible mechanism of film formation in a discharge. On the basis of this type of mechanism, Haefer has calculated $p_1 = dp/dt$, the number of molecules entering a layer of the film of area 1 cm² in 1 s. If N molecules are adsorbed on 1 cm² of the electrode, we have

$$p_1 = \sigma \cdot j \cdot N \qquad (1)$$

where j is the number of charged particles on 1 cm² after 1 s, and σ the ionisation cross-section of a sorbed molecule on electron or ion impact. Let us consider two extreme cases, in which (1) the vapour pressure ensures a complete monolayer, or (2) the monolayer is incomplete.

In the former case the partial pressure of the starting material is quite high. The number of molecules F of the gas phase incident on unit surface in 1 s is then large compared with the rate of film formation p_1. During the first few moments the surface becomes covered with a monolayer: $N = 1/a$, where a is the surface necessary for the adsorption of one molecule. In this case the rate of growth of the polymer film is

$$p_1 = \frac{\sigma}{a} \cdot j. \qquad (2)$$

Experimental support for this conclusion has been given by Haefer and Mohamed [77].

If the number of adsorbed molecules is even less than a monolayer, i.e. if $N < 1/a$, we have

$$\frac{dN}{dt} = F - \frac{N}{\tau} - p_1 = F - \frac{N}{t} - \sigma j N = 0 \qquad (3)$$

where τ is the life of an adsorbed molecule. From Eqn. (3) we find that

$$N = \frac{F}{\sigma j + \frac{1}{\tau}} \qquad (4)$$

and from Eqns. (1) and (4) we obtain

$$p_1 = \frac{\sigma j F}{\sigma j + \frac{1}{\tau}} = \frac{F}{1 + \frac{1}{\sigma \tau j}}. \qquad (5)$$

Two cases can be distinguished:

$$1) \quad \sigma\tau j \ll 1, \text{ then } p_1 = \sigma\tau j \cdot F \qquad (5a)$$

i.e. at low current densities and with small interaction cross-sections the rate of growth of the polymer film is proportional to the current density and the vapour pressure.

$$2) \quad \sigma\tau j \gg 1 \text{ then } p_1 = F \qquad (5b)$$

i.e. at high current densities and with a large interaction cross-section the rate of growth reaches a limiting value: every molecule striking the electrode enters the polymer. This theory is supported by measurements made with oil molecules under conditions of electron impact [24,30,32,45].

A somewhat different mechanism for the formation of coating films in the glow discharge is suggested by Haisen [78], who assumes that the layers are formed from fragments produced, not in the gas space, but directly on the surface of the object. Particles incident on the surface, and carrying excess energy, split up the adsorbed hydrocarbon molecules, and the resulting fragments recombine to form a solid deposit. However, the author does not give sufficiently convincing experimental evidence in support of this view.

Film formation in a discharge has been studied not only with hydrocarbons which are incapable of ordinary chain polymerisation but also with typical monomers. Rubanovskii [79] studied the kinetics of the polymerisation of butadiene in the glow discharge, and observed the deposition of a solid polymer on the walls of the discharge tube and on the electrodes. He showed also that polymerisation is excited not only by the impact of electrons but also by that of hydrogen atoms. The process of polymerisation exhibits a clearly marked induction period.

The discharge polymerisation of one of the most widely investigated monomers, styrene, has been studied by Stuart [58], who obtained polystyrene films insoluble both in water and inorganic solvents. Electron spin resonance measurements, made in a vacuum at room temperature, showed the presence of free radicals, which most probably underwent oxidation to peroxide in air.

The production of solid polymers from several typical monomers in a discharge has been referred to in other papers [56,57,60,73]. However, it is only recently that the behaviour of typical monomers and polymers in a discharge has begun to be studied more thoroughly.

DaSilva and Miller [63] studied the rates of formation of polymer films from butadiene and vinyl chloride. They showed that, after the discharge has operated for 3 min, butadiene gives a film 400 Å thick at a gas pressure of 100 mmHg, whereas with vinyl chloride the rate of deposition is 30 Å s^{-1} (if the discharge current is 70–90 mA, and the voltage 100–150 V). The electrical properties of polybutadiene films obtained in a discharge (pressure 0.3–0.55 mmHg, voltage 350–400 V, and current 6–8 mA) have been studied by Bashara and Doty [66], who assume the films to consist of poly-1,4-butadiene and to be extremely strongly cross-linked. They found the resistivity of such films to be $\sim 10^{11}$ ohm cm.

Holland [80] studied the behaviour of several polymeric materials—polyethylene, polystyrene, epichlorohydrin resin, cross-linked melamine—in a discharge of voltage 5 kV and current density 0.13 mA cm^{-2} with cooled specimens in an atmosphere of air or argon. He showed that the cathodic samples became brown and non-transparent 50 min after the start of an experiment. Under the action of electrons the specimens underwent surface pitting, and ions sometimes caused "erosion" of the surface.

The action of a discharge on the surface of polymer films led to the idea that a polymer might be activated in a discharge with the aim of subsequent grafting. Korshak et al. [65] used the activation of polytetrafluoroethylene in a discharge in order to initiate on its surface the graft polymerisation of vinyl monomers with the object of improving the adhesive properties of the material. Special apparatus was used for a discharge of frequency 50 c/s and voltage 22–30 kV. The film obtained from tetrafluoroethylene was placed in the discharge zone for 10–30 min, then immersed in a vessel containing the vinyl monomer, and copolymerised at 85–90°C. Such grafting considerably improved the adhesion of the polytetrafluoroethylene to steel and other materials.

The production of films in a glow discharge is of very considerable value for the recently started wide application of silica and organosilicon films as surface passivators and diffusion coatings in microelectronics.

Leslie et al. [81] studied the low-temperature deposition of silica films, for which purpose an organic silicone (an

alkoxysilane) was decomposed in an argon plasma. Breakdown of the silicone molecules on collision with ionised and excited argon atoms took place on the electrode surface, where a stable Si–O–Si lattice was formed. The rate of deposition was studied as function of the flux of ions, the power of the discharge, the temperature, and the geometry of the substrate. The resulting silica films were studied by various methods: electron diffraction confirmed their amorphous structure, and the infrared spectra showed the absence of C–H bonds. Ing and Davern[82] also prepared silica films for coating semiconductors. Deposition was conducted in tetraethylsilane vapour in a glow discharge. The resulting film was homogeneous, and possessed good adhesion to a gallium arsenide surface. Such a film was 1800–2000 Å thick. These workers have subsequently investigated[83] thin silica films obtained from tetraethoxysilane in a discharge. These films can be successfully used as dielectrics in thin-film capacitors.

IV. PRODUCTION OF POLYMER FILMS ON EXPOSURE TO ULTRAVIOLET RADIATION

The chemical processes occurring under the influence of ultraviolet radiation, and leading to the formation of polymeric deposits on solid surfaces, resemble in many respects the analogous processes occurring on electron bombardment. It must be noted, however, that photochemical investigations in this field, which were begun in 1910 and continue at the present time, have mainly been purely descriptive and qualitative in character.

In 1910 Berthelot and Gaudechon[84] observed the formation of polymeric solid deposits on the walls of the reaction vessel when acetylene was exposed to ultraviolet radiation. The yellow film obtained was similar in appearance to that formed by the action of a discharge on acetylene. Even certain kinetic aspects of the formation of films of this kind were noted: the rate of deposition of films slowed down in the course of growth owing to absorption by them of ultraviolet radiation, and the rate of conversion of acetylene into solid polymer was approximately doubled in the presence of an inert gas.

Lind and Livingston[85], while studying the photochemical polymerisation of acetylene, observed the deposition of a solid polymer on the window through which the ultraviolet irradiation occurred, this resulting in diminished transparency of the window and a fall in the rate of polymerisation.

Bates and Taylor[86] and also Reinicke[87], while investigating the photoexcitation of ethylene and acetylene, also noted the formation of a solid polymer, insoluble in organic solvents.

Olson and Meyers[88] obtained polymeric solid deposits on the walls of a reaction chamber in which ethylene had been subjected to ultraviolet irradiation. The deposits were detected from the interference colours and also from the effect on the rates of subsequent reactions. Kemula and Mrazek[89] studied the mechanism of the photopolymerisation of acetylene, and found among the many polymerisation products a yellowish solid deposited on the walls of the reaction vessel. This substance absorbed the active part of the radiation very strongly, and diminished the reaction velocity. Livingston and Schiflett[90], who studied the photopolymerisation of methylene at high temperatures, detected two non-volatile solid products, one of them resembling cuprene, while the other formed a film recalling a dark yellow dried lacquer film. On heating the film charred, but it burned in air only with difficulty, forming a compact coating which adhered well to the surface. This film was partly soluble in ether, which was coloured a dark yellow. Melville[91] showed that the maximum permissible gas pressure in the vessel during the photochemical polymerisation of ethylene and acetylene was 10 mmHg, since at higher pressures deposits of a solid polymer were formed on the walls of the reaction vessel. The formation of solid films during the photopolymerisation of acetylene was noted also by Le Roy and Steacie[92]. The films could be removed by burning them off after an experiment. Numerous studies of the photopolymerisation of acetylene and ethylene were collated in Steacie's book[93], but in nearly all of these the authors had merely noted the formation of solid polymer films and described their properties sketchily. Nevertheless, even in the more recent work of the 1950s and 1960s the preparation of polymer films by ultraviolet irradiation has not been a subject of independent study. Zelikoff and Aschenbrand[94], while investigating the photochemistry of the vacuum ultraviolet, noted the formation of a solid polymer on the walls of an acetylene reaction vessel, and the consequent diminution in its transparency. The coating which had absorbed the ultraviolet radiation was formed in about 3 min. The resulting film was decomposed by nitric acid. DeCarlo et al.[95] also noted the formation of solid polymers by the ultraviolet irradiation of acetylene.

Although the polymer films formed on a solid surface by the action of ultraviolet radiation have not become a subject of independent study, several authors have nevertheless suggested possible mechanisms for their formation. Whereas in the early papers of the 1930s preference was given to a mechanism involving excited molecules, Steacie[93] was inclined to adhere to a free-radical mechanism.

All workers who have observed films of this type on ultraviolet irradiation have noted their good adhesion to the surface on which they had been deposited, their high thermal stability, and their resistance to many solvents.

V. APPLICATION OF FILMS

It has been shown above that polymer films obtained by the action of electrons and in a glow discharge possess good dielectric properties. They possess also great strength, good surface adhesion, high thermal stability, and a lack of pores. The method permits very thin films to be obtained. All this suggests that the use of such films as dielectric layers in capacitors is very promising. Several patents[61,68,69] have proposed the use for this purpose of polymer films obtained in a discharge. Use of polymer films of this type permits a considerable increase in the capacitance per unit volume of the condenser and a substantial decrease in the size of the latter. Other methods of obtaining thin (around 1–2 μm) dielectric films have been tried[68], but none has given good results, mainly because the capacitors rapidly became defective owing to breakdown of the dielectric layer. The poor quality of the films—presence of pores, and also various types of impurities—proved to be the cause of the breakdowns. These defects are absent in polymer films obtained in a discharge, since the dielectric layer is then obtained directly on the surface on which it is to be used. A great advantage of capacitors made with films obtained in this way is also their excellent temperature stability, for they

can work at temperatures from −55° to +200°C.[68] A British patent[68] proposes the use as dielectric layers of polymer films 0.01–1 μm thick obtained from unsaturated aromatic or aliphatic compounds in a glow discharge. To obtain organic films of specified thickness in this case, a synthetic, e.g. polyethylene, film, which has first been coated with a thin layer of aluminium, is drawn through the discharge zone at a constant speed, which determines the thickness of the newly formed film if the discharge parameters are kept constant. A second layer of metal is applied to the resulting film by sputtering. The conditions of the discharge comprised an optimum pressure of the organic substance in the discharge zone of 10–100 μm, and an ignition voltage of the discharge of 300–2000 V. Either direct or alternating current can be used to obtain the dielectric films. A necessary condition for the production of homogeneous films is the presence of a steady visible discharge in the region between the electrodes.

Various methods of obtaining dielectric films in capacitors, including use of a glow discharge, have been surveyed[96], and use of polytetrafluoroethylene films obtained in a glow discharge as dielectric layers is claimed to yield excellent thin-film capacitors[97]. Coleman[61] and the Radiation Research Corporation[67] have suggested designs for special apparatus for the production of homogeneous and especially thin polymer films in a discharge, which can be used for the manufacture of capacitors. Hopf[98] states that polymerisation in a discharge is one of the cheapest methods for obtaining capacitor layers and protective coatings.

It has been suggested[99,100] that polymer films, formed on a surface under the influence of a glow discharge, might be used as anticorrosive protective coatings. Production of the coatings involves preparing the film itself, hardening it, and drying it at a definite temperature. Styrene and other monomers of the vinyl series have been used as film-forming material. The metal to be coated with a protective film was used as electrodes in the discharge chamber at a voltage of 300–1000 V. Coatings 0.1–0.5 mm thick were obtained. A typical consumption of electrical energy is 1 kW h for the production of 50 g of film. Sandford[99] has compared the properties of metallic and non-metallic protective coatings on metals, including polymer films applied in a discharge, and has reached the conclusion that the polymer coatings fully replace the former and, moreover, are cheaper.

Buck and Shoulders[101] proposed the use of films, obtained from organic substances by the action of electrons, as dielectrics in microelectronic circuits. These films can probably be utilised both for the manufacture of microcapacitors and to protect the final circuit from the atmosphere. An analogous application of polymer films has been mentioned elsewhere[37]. The semiconductor films obtained by Christy[25] point to the possibility of producing film diodes, and study of the mechanism by which current flows through very thin polymer films[48,49] shows that it is possible in principle to make thin-film tunnel triodes.

The method of applying polymer coatings in a glow discharge has been used for a long time to obtain replicas from small objects in electron-microscopic investigations[64,70]. The method consists essentially in coating the surface of the object which is to be examined in the electron microscope with an organic film, using benzene vapour in a glow discharge. The object is then heated in a high vacuum to 400°C, when the organic film is converted into a carbon film. After this the material of the object itself is decomposed chemically, so that only the carbon sheath remains, which is penetrated strongly by the electron beam. This method enables the finest surface details of particles to be observed.

The production of polymer films by the action of electrons has been proposed[102,103] for the manufacture of diffraction gratings, and also[45] for the production of optical interference filters.

Hirsch[42] suggested using this phenomenon, of the deposition of a polymer film on a surface bombarded with electrons, for focussing beams in the design of electronic apparatus. At points bombarded by electrons images are obtained, invisible to the eyes, caused by the formation of very thin polymer films. This latent image can be made visible by developing it by electrodeposition in copper sulphate solution. This method of obtaining the focal characteristics of an electron beam makes it possible to obtain images even with electrons of very low energies (up to 5 eV).

Bradley[75] has shown that polymer films obtained in a discharge possess great photosensitivity. This had again been pointed out by Mayer[38], who had investigated films obtained under the influence of an electron beam, and found them to possess photosensitivity in the visible and near infrared region. These properties of the films can be utilised in photosensitive high-temperature detectors[74].

Woodman[43] has proposed the use of silica films as diffusion masks for protecting a germanium surface from the diffusion of indium and antimony into it, which may be of value in the production of germanium diodes and triodes. In this work the silica films were obtained by electron bombardment of a germanium surface on which a thin film of phenylsilanol had first been condensed from the vapour. The resulting polymer film was oxidised in air at 500°C until pure silicon dioxide was obtained. It was found that a silica film on the germanium surface was completely impermeable to antimony, but permeable to indium.

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In the present paper we have summarised published information on the formation of polymeric organic films on solid surfaces by the action of active particles. A survey of the information given here shows that researches in this field have been quite widely developed in several countries, and even have already found practical application in the production of protective coatings and thin-film condensers, which possess high specific capacitance. The method discussed in this paper appears to us to open up several novel and interesting technical possibilities, and merits the attention of research workers in our own country.

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THE USE OF RADIOACTIVE INERT GASES IN THE STUDY OF SOLIDS

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1. INTRODUCTION

The development of work on the study of solids requires the use of sensitive methods of various types for the study of phase transitions, chemical changes, the production of imperfections and defects in the crystal lattice, changes in the properties of a surface, etc.

In addition to physical methods of study, the use of radiochemical methods is of interest; in these methods, the liberation of radioactive inert gases makes it possible to follow continuously various types of change taking place during processes in a solid at the temperature of the experiment. The general term "emanation" is often used to denote the radioactive inert gases formed in nuclear reactions, and the methods of study based on the introduction of a radioactive inert gas into a solid and subsequent measurement of the fraction of emanation liberated or the emanating power of the substance are usually described as emanation methods.

The classical emanation method, using natural radioactive inert gases, was suggested by Kolovrat-Chervinskii[1] and subsequently developed and improved by Hahn[2], Zimens and Flügge[3,4], and Starik[5]. Various modifications of this method are now known[6-8], based on the use of radioactive isotopes of the inert gases.

Work on the theory and application of the emanation method in the study of reactions in solids has been reviewed in papers by Hahn[2,9] and in a monograph by Wahl and Bonner[10].

In recent years, in connection with the development of work on the peaceful uses of atomic energy and new problems in the physical chemistry of solids, a large number of papers have been published on the use of different versions of the emanation method in the study of solids. At the same time there has been a marked increase in the range of problems studied by emanation methods, and in many cases these methods are combined with X-ray diffraction, thermographic, dilatometric, and sorption methods; this makes possible a more unambiguous interpretation of the results obtained[11-13].

2. THEORETICAL PRINCIPLES OF EMANATION METHODS. METHODS OF INTRODUCING AND MEASURING RADIOACTIVE INERT GASES

The emanation method is fundamentally different from other radiochemical methods; the classical version of the method is based on the properties of various radioactive elements, such as radium, thorium-X, and actinium-X, which disintegrate with the liberation of radioactive noble gases or emanations, which may be quantitatively determined with a high accuracy from their α-radiation. Less frequently, the β-radiation of the active residue from the emanation is measured[2]:

$$^{228}\mathrm{Th\,(RdTh)} \xrightarrow[5.4\ \mathrm{MeV}]{\alpha} \mathrm{ThX} \xrightarrow[5.7\ \mathrm{MeV}]{\alpha} {}^{220}\mathrm{Em\,(Th)} \xrightarrow{\alpha} {}^{216}\mathrm{ThA} \xrightarrow{\beta} \ldots$$

The method involves the introduction, into the solid being studied, of a mother isotope (Ra, RdTh, AcX), which generates emanation continuously by radioactive disintegration, followed by the measurement of the proportion of radioactive noble gas capable of being liberated from the specimen under certain conditions[4,10]. This liberated fraction of the emanation or the emanating power of the given substance is in general a function of the temperature, surface area, and state of the crystal lattice of the solid. The term emanation coefficient is generally used to denote the ratio of the fraction of the emanation liberated to the total quantity of emanation formed in the test specimen when a steady state is established. Since the radioactive gas liberated is inert and does not react with the solid, the results obtained are not complicated by any side chemical reactions.

The classical emanation method was developed chiefly by the work of Kolovrat-Chervinskii, Hahn, Zimens, Flügge, Starik, and others. The most complete theory of emanation was first given in papers by Flügge and Zimens[3,14,15], who emphasised the existence of two fundamentally different mechanisms for liberation of atoms of the emanation. The first involves that fraction of the atoms which is liberated directly as a result of the recoil energy on radioactive disintegration of the radioactive mother element, and the second involves the atoms of emanation formed within the solid and liberated by diffusion through the vacant sites, capillaries, and cracks in the solid. The values of the emanating power due to the processes of radioactive recoil and diffusion are denoted by the symbols E_0 and Ed respectively. Thus the total emanating power of a specimen determined experimentally, which is usually denoted by the symbol EV, consists of two parts: $EV = E_0 + Ed$. Zimens examined the liberation of emanation both from a single particle[15] and from an aggregate of particles[14]. A recoil atom from a particle will be liberated only when the mother element is situated at a distance x which does not exceed the recoil free path R. The average fraction of atoms formed in the range R from the surface will then be given by the ratio of the volume in which the atom of emanation is formed to the total volume.

The average fraction of atoms formed at a distance $x < R$ from the surface and ejected from the particle is

$$\frac{\int_0^R \frac{2\pi R(R-x)}{4\pi R^2}\,dx}{R} = \frac{\int_0^R \frac{R-x}{2R}\,dx}{R} = {}^1/_4 . \quad (1)$$

Thus

$$E_0 = {}^1/_4 \cdot \frac{R \cdot S}{v},$$

where S is the surface area, and v the volume of the particle, or

$$E_0 = \frac{R}{4} \cdot \rho \cdot \frac{S}{m}, \quad (2)$$

where ρ is the density and m the mass of the particle.

This is applicable to particles with dimensions $\geq 10^{-4}$ cm. The diffusion component of the emanation will in general depend on the diffusion coefficient D for the inert gas through the solid and the radioactive decay constant λ for the emanation.

Zimens[15] put forward the equation

$$E_d = \sqrt{\frac{D}{\lambda}}\,\rho\,\frac{S}{m} . \quad (3)$$

Thus

$$EV = E_0 + E_d = \left(\frac{R}{4} + \sqrt{\frac{D}{\lambda}}\right)\rho\,\frac{S}{m} . \quad (4)$$

When the process of emanation for an aggregate of particles is considered, it is also necessary to make allowance for the indirect effect of the recoil produced when the recoil atom collides with a neighbouring particle in the solid. For particles smaller than 1 μm, the distances between the particles generally do not exceed the recoil free path, and the atoms of emanation are liberated chiefly as a result of the indirect effect of the recoil. The proportion of these atoms is a sensitive function of the composition of the solid and of the presence of various impurities. A paper by Götte[16], for example, reports an increase in the emanation of thoron from zinc hydroxide from 22% to 60% when inactive iron hydroxide is added. The development of a theory of the process of emanation for an aggregate of particles is complicated by the need to make allowance for the length and diameter of the pores, the ratio of the volume of the pores and the volume of an individual particle, and the possible adsorption of emanation on the surface of the particles.

The practical utilisation of Eqns. (1)–(4) requires a knowledge of the magnitude of the recoil free path R, for which Flügge and Zimens[3] put forward the equation

$$R = g\,\frac{1}{\rho}\left(\frac{\overline{AB}}{s}\right) \quad (5)$$

where g is a proportionality factor, ρ the density, and $\overline{AB}/s$ the mean ratio of the atomic weight to the stopping power of the solid, which Flügge and Zimens[3] assumed, without sufficient justification, to be equal to the stopping power of the solid with respect to α-particles[17]. Flügge and Zimens also assumed that the recoil free path R was proportional to the square of the recoil energy ϵ_0:

$$R \propto C\epsilon_0^2. \quad (6)$$

To calculate the proportionality factor g in Eqn. (5), it is necessary to determine the emanating power due entirely to recoil. This can be done, for example, by measuring the coefficient of emanation for the liberation of two forms of emanation with different half-lives, or by measuring the temperature coefficient of emanation[10]. For radon and thoron the constant g can be found directly by measuring the emanating power of glass rods with known dimensions[18]. The values of the factor g are 57×10^{-8} for radon and 74×10^{-8} for thoron.

If it is assumed that all the recoil atoms are liberated immediately after formation and that their rate of liberation is independent of the quantity of inert gas in the specimen, the measured emanating power for a freshly prepared specimen will be due almost entirely to recoil. The diffusion component, however, will be a function of the total concentration of gas and the age and temperature of the specimen. Since the recoil energy for α-radiation is of the order of 100 000 eV, whereas the thermal energy amounts to ~ 0.1 eV, the recoil emanation is almost independent of temperature, and the temperature coefficient of the evolution of emanation is determined by the diffusion component[10]:

$$E_d = Ae^{-\epsilon_{EV}/RT} \quad (7)$$

where ϵ_{EV} is the activation energy of the emanation process. It should be noted that the applicability of Eqns. (2)–(6) is limited, since they make no allowance for side processes such as adsorption, the indirect effect of the recoil, and possible changes in the specimen itself.

Baulch and Duncan[19] compare calculated and experimental values of the recoil free path for atoms of emanation, obtained from the equation of Flügge and Zimens[15] and from their own formulae[19]. They consider that both of Zimens' equations—formulae (5) and (6)—which give the relationship between the length of the free path and the energy of the recoil atoms, are unsatisfactory. From Bohr's classical equation[20] for the adiabatic collision of a recoil atom with an atom of the retarding gas

$$R_0 = \frac{m_e\,\epsilon}{\pi N \hbar^2 Z_1^{2/3} Z_2} \quad (8)$$

(where m_e is the mass of the electron, N is the number of atoms of the stopping material in 1 cm^3, Z_1 and Z_2 are the nuclear charges of the recoil atom and the colliding atom respectively, R_0 is the mean free path of the recoil atom, and ϵ is the energy of the recoil atom), Baulch and Duncan put forward an equation for calculating the number of recoil atoms with free path length R.

These workers[19] determined the free path and the energy of the recoil atoms for ThC″ and RaA. The recoil atoms moved a known distance from the source to a metal collector plate through a gaseous stopping medium, whose pressure was measured with high accuracy. The activity of the collector plate was then measured with a Geiger counter. In the treatment of the results, allowance was made both for the geometric factor (i.e. the dependence of the number of recoil atoms reaching the plate on the geometry of the apparatus used) and for the degree of straggling (i.e. the deviation of the free path from its mean value). Allowance for these factors in the comparison of theoretical and experimental results leads, in their opinion[19], to satisfactory agreement with experiment. Thus for thoron with a recoil energy of 103 keV, the calculated mean free path in air at atmospheric pressure is 0.059 cm, while the value found experimentally[3] is 0.083 cm; in barium stearate the calculated free path is 960 Å, while that determined experimentally is 940 Å.[21]

The recoil energy ϵ_R was calculated from the equation

$$\epsilon_R = 4\epsilon_\alpha/M \quad (9)$$

where ϵ_α is the energy of α-decay, and M the mass of the recoil atom.

In conclusion, Baulch and Duncan[19] point out that formula (8) gives better agreement with experiment than do Eqns. (4)–(6), proposed by Flügge and Zimens, since the mean free path of the recoil atoms is proportional to the recoil energy to the first power—rather than to the square—of the recoil energy. Moreover, Eqn. (5) was derived without allowance for the degree of straggling, which depends on the stopping medium, and on the unjustified assumption that the stopping power of a substance is the same with respect to α-particles and to recoil atoms. It should be noted that there are a large number of systems for which the theoretical calculation of R_0 does not give satisfactory agreement with experiment, and further fairly complicated experiments are required, so that most authors dealing with the emanation method restrict themselves to a qualitative treatment of the results obtained.

The choice of method for the introduction of the emanating radioactive mother element and the nature of its distribution in the solid being studied are very important in the emanation method. This problem was examined in some detail by Zimens[4], who demonstrated the possibility of a uniform distribution of the radioactive element for most precipitates with an extensively developed surface, even when there is no isomorphism. He also described various types of emanation–temperature curves, which have generally figured in all subsequent studies using the emanation method. These curves are of the following types—(1) temperature curves (LT) obtained by measuring the emanating power EV with continuous rise in the temperature of the specimen; (2) temperature curves (RT) obtained by measuring EV after the heating has been interrupted at a given point and the specimen cooled; (3) isotherms, representing the dependence of EV on time or specimen weight at constant temperature; (4) cooling curves characterising EV directly during the cooling of a specimen previously heated to a high temperature; and (5) duplicate curves obtained by measuring the emanation of a specimen during repeated continuous increase in temperature at a given rate.

Later work using the classical emanation method demonstrated that the temperature variation of EV was almost completely unaffected by two methods of introducing the original mother isotope into the test solid (coprecipitation and impregnation). The introduction of radiothorium by the impregnation of a previously prepared precipitate of the test solid generally leads to higher absolute values of the emanating power compared with specimens labelled with radiothorium during precipitation, but does not alter the nature of the variation in EV with temperature. This has been shown by Zhabrova and Shibanova[22,23], who impregnated magnesium and zirconium hydroxides with aqueous solutions of radiothorium, and also by Zaborenko and Tetner[24], who impregnated inorganic salts with alcoholic radiothorium solutions.

In addition to the classical version of the emanation method, various modifications of the method are now used, distinguished chiefly by a fundamentally different method for introducing the radioactive inert gas into the solid being studied. Characteristic features common to all these methods are that the radioactive inert gas is liberated only by diffusion and is not replenished on liberation, so that allowance must be made for its decay with time.

One of these modifications of the classical emanation method is the method of surface radioactive gas labelling, developed by Jech in Czechoslovakia[6,25,26]. In this method, the radioactive inert gas—radon, xenon (^{131}Xe), or krypton (^{85}Kr)—is introduced into thin surface layers by ion bombardment of the surface of the solid in a high-frequency discharge[6]. The depth of penetration into the solid amounts to 10–30 Å. Both the quantity of radioactive gas introduced into the surface of the specimen, and the rate of its liberation, depend on the structure and the state of the surface. This was first used to study the thermal decomposition of nickel oxalate and to examine the surface of glasses subjected to different treatments[25]. Unlike the emanation method, which is based on the continuous formation of radioactive inert gas inside the solid, the method of surface gas labelling is based on the introduction of a definite limited quantity of radioactive gas; as already noted, the radioactive atoms penetrate to a very shallow depth, and can be liberated only by diffusion. This labelled-surface method can be used to determine the topography of various surface structures, and also to observe the course of surface chemical reactions, which alter the rate of evolution of the surface gas label.

Another method for introducing the emanation was proposed by Lindner[8]. It is based on the introduction of atoms of radium emanation (radon) into the surface of the solid being studied, by recoil when the specimen is placed in $^{226}RaCl_2$ solution. The radon penetrates to a depth of 100–150 Å, and the remaining radium chloride is removed by washing. With a sufficiently small particle size ($\sim$ 0.5 μm) the atoms of the emanation are distributed uniformly throughout the substance. The need to bring the test specimens into contact with solution and water undoubtedly restricts the possible applications of this method for introducing a radioactive noble gas into a solid surface.

The principle for utilisation of the emanation method proposed by Yajima and others[7,27] is closely related to those described above. Radioactive isotopes (xenon, krypton, etc.) were used, but they were introduced into the solid by mixing it with uranium dioxide and then irradiating the mixture with thermal neutrons. Thus, as a result of the recoil energy, the radioactive inert gases, which are fission products, are trapped by the surrounding powder[28], and their rate of liberation is determined by the state of the crystal lattice of the solid. A correlation was established[27] between the evolution of gaseous fission products and changes in the crystal structure of various specimens of haematite. Yajima et al.[27] prefer this method of introducing the radioactive gas, since it eliminates chemical treatment and can be applied to many solids, including metals. It should be noted that the specimens may exhibit induced activity, and this may introduce difficulties into subsequent work.

In all these varieties of the emanation method, the radioactive gas is present in the solid as a result of radiation effects. In the classical version, when the radioactive isotope of thorium ^{228}Th is introduced into the test solids, the ThX and then the thoron, formed by successive radioactive disintegration, penetrate into the lattice of the solid as a result of the recoil energy.

The radioactive gas label (Rn, ^{85}Kr) is introduced into the lattice of the solid by ion bombardment in an electrical discharge, etc. Thus the principle of the introduction of the radioactive gases is essentially radiative. Until recently, however, no work had been done making use

of different versions of the emanation method to study the same materials. Thus comparison of results obtained on the thermal decomposition of hydroxides[23] and oxalates[29], obtained by the classical emanation method and by surface gas labelling, are of undoubted interest; this comparison has shown that, for the simple topochemical processes of the conversion of hydroxide into oxide, the extremal points for the liberation of the emanation and the radioactive gas label generally coincide. There obviously should not be a sharp difference between these methods, since, as noted above, the radioactive gas is in all instances present in the lattice of the solid as a result of radiation effects. In the former case, however, the radioactive gas produced is present—according to calculations based on the formula of Flügge and Zimens[3]—at a depth of 300–400 Å and is generated continuously. In the latter case the radioactive gas is present at a depth of several dozen Ångström units, and is not replenished on liberation. Thus in some instances the fixation of high-temperature processes by the method of surface gas labelling is difficult, so that the thermally activated liberation of the radioactive gas, due to diffusion, and the state of the surface of the specimen before the deliberate introduction of the radioactive gas label, acquire considerable importance. Moreover, the surface layer may be broken down on the introduction of radioactive atoms of radon or krypton, and some of the radioactive gas is liberated during the annealing of the defects at 50–100°C, Thus the fairly broad low-temperature peaks for the liberation of ^{85}Kr, observed e.g. in the decomposition of oxalates[29], can be assumed to be due to thermal diffusion with simultaneous partial dehydration. These characteristic features of the methods possibly explain the differences observed[29] in the study of more complicated multistage processes, e.g. the decomposition of oxalates. Further deeper and more detailed comparison of different versions of the emanation method with different treatments of the solids being studied is of interest: it may give new information on fine changes in their structures and surfaces.

The use of the emanation method in most instances requires continuous recording of the α-activity of the inert gases (radon, thoron, and actinon) with time.

The flow method for measuring the quantity of emanation liberated has been described in detail[9,30,31]. The basic scheme used in the measurements is shown in Fig. 1: the inert carrier gas is passed at a definite rate from the purification and drying system into a reaction vessel, which is placed in a furnace and contains a known weight of the test substance, after which it passes together with the liberated fraction of the emanation through a system of traps and driers into the measuring chamber of the recording instrument. The procedure used in the measurements has remained basically unchanged. The changes introduced have been concerned with improving the design of the measuring chambers and of the counting and recording apparatus.

Many authors[30,32-34] have used ionisation chambers of volume 200–600 cm^3 as detectors for measuring α-activity. The conditions for measuring thoron and actinon by means of an ionisation chamber have been examined in most detail by Voltz and Adloff[35], who give equations relating the rate of flow of carrier gas with the distance from the chamber to the emanation source and with the geometry of the apparatus used, and also discuss in detail the influence of traces of moisture and organic substances on the conditions of ionisation in the chamber. Traces of

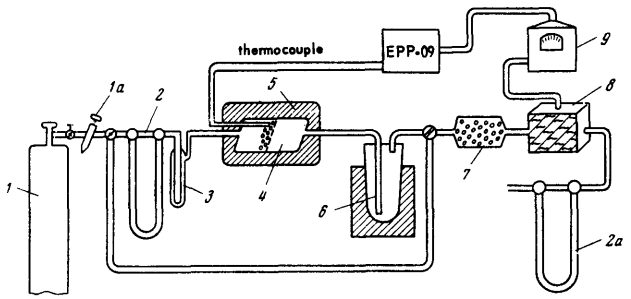


Fig. 1. Basic scheme for measuring the emanation of solids in a current of inert carrier gas:
1) cylinder containing inert carrier gas; 1a) fine control valve; 2, 2a) flowmeters to measure rate of flow of carrier gas; 3, 6, 7) system of traps for purifying and drying the gas being passed through; 4) reaction vessel containing test substance; 5) electric furnace; 8, 9) measuring chamber and recording instrument for determining and automatically recording the quantity of radioactive inert gas liberated.

organic substances generally influence the rate of collection of the ions formed, as a result of changes in their mobilities. This has been demonstrated by Roginskii and his coworkers[36]. Only hydrogen had almost no influence on the degree of ionisation, acetone vapour increased it, and isopropyl alcohol and propene decreased it by 20–40%. The use of ionisation chambers ensures high efficiency and high sensitivity (10^{-11}–10^{-13} c) in the measuring instruments used. A complicating feature in this instance is the need for fairly complicated electronic apparatus to measure the small ionisation current. Because of the high sensitivity of the electronic recording assemblies, thorough elimination of mechanical, electrical, and magnetic interference is necessary. Thus in recent years most workers[12,13,25] have begun to use scintillation counters with measuring chambers of different designs for measuring the α-activity of the emanation. This apparatus is more simple and stable in operation, and is almost unaffected by impurities in the carrier gas, but it requires slightly greater activities, since the efficiency of the assemblies used generally does not exceed 20%. At the same time, certain difficulties are encountered in the elimination of the "radioactive memory" of the scintillation measuring chambers.

Ordinary paired end-face counters are used to measure the β- and γ-activities of krypton, xenon, and other radioactive inert gases[26,37].

3. EMANATING POWER AS A FUNCTION OF THE SPECIFIC SURFACE OF SOLIDS

Although Kolovrat-Chervinskii[1] was the first to examine in detail only the conditions of liberation of emanation, Hahn[2,9,38] pointed out various possible promising applications of the emanation method to the study of physicochemical changes taking place in solids. Hahn first used the emanation method to study the surface of metal hydroxide gels and the changes in it during aging and dehydration[39]. Hahn[40] subsequently studied the change on heating occurring in the surface of $Fe_2O_3 \cdot xH_2O$ labelled with RdTh,

and noted the high emanating power of the original hydroxide due to the presence of an extensively developed internal surface in $Fe(OH)_3$ (Fig. 2). The initial decrease in the emanation, measured at the temperature of the experiment or at room temperature, was attributed to "aging", which masks the increase in emanating power due to the removal of water vapour, which entrains thoron. With careful heating or preliminary drying, the relationship between these processes can apparently be reversed. Above 400°C rapid crystallisation of the highly disperse gel takes place, with the evolution of a large quantity of heat, and this naturally leads to a decrease in surface area and to a more rapid decrease in the emanation. The subsequent increase in emanating power at 800°C was attributed[40] to the liberation of traces of water trapped inside the crystal lattice during precipitation of the gel from the colloidal solution. At 1000°C secondary ordering of the lattice is observed, leading to smoothing of the surface and an increase in the size of the particles of iron oxide formed. The temperature of the start of these processes, which can be determined accurately by the emanation method, was called the break temperature (*Knietemperatur*) by Hedvall[41]. The marked increase in the emanation above 1080°C is due to the increase in the mobility of the atoms or ions forming the crystal lattice. As pointed out by Tammann[42], for many powdered crystalline substances the temperature of the start of appreciable displacement of the atoms or ions in the lattice and increase in the rate of diffusion of the atoms between the crystalline solids in the case of a mixture of powders is close to 50–60% of the absolute melting point of the given substance, provided that no phase changes occur above this temperature (termed the Tammann temperature). Thus by studying the variation in the emanation with temperature it is possible to determine the Tammann temperature, above which reactions in the solid state become possible. The emanation method was used also[40] to study the behaviour of iron(III) oxide subjected to different treatments, and the temperature variation in the emanation of thorium oxalate and hydroxide was given for comparison. The emanation was not measured continuously, however, and the specific surface of the materials studied was not determined; these are unsatisfactory features of the work cited.

Hahn[2] also made an extensive study of the dependence of the emanation of various glasses on the state of their surfaces. Strassmann[43,44] observed an increase in the emanation coefficient for the barium salts of monobasic aliphatic acids with increase in the length of the carbon chain; for barium palmitate the emanation coefficient amounted to 100%. These substances, like various metal hydroxides with an extensively developed internal surface and hence a high emanation coefficient, found application in nuclear physics for the separation of short-lived decay products[45]. More detailed studies of the dependence of the emanation of inorganic salts and minerals on the state and "preservation" of their salts were made by Khlopin[46] and by Starik and Melikova[47]. These studies showed that the dependence of the emanation coefficient on the specific surface for various radon isotopes could give information on the form in which the radioactive mother substances were present in the solid; this in itself is very important for radiochemistry. An attempt to measure the surface area of cubic crystals by measuring the free path of emanation recoil atoms was made by Kurbatov[48] and later by Flügge and Zimens[49] on the basis of Eqns. (2)–(5) given above.

If radium isotopes yielding radon and thoron on radioactive decay are introduced into the specimen being studied, we have, from Eqn. (3),

$$\left.\begin{aligned} EV_{Rn} &= \left(\frac{R_{Rn}}{4} + \sqrt{\frac{D}{\lambda_{Rn}}}\right)\rho\frac{S}{m} \\ EV_{Tn} &= \left(\frac{R_{Tn}}{4} + \sqrt{\frac{D}{\lambda_{Tn}}}\right)\rho\frac{S}{m} \end{aligned}\right\} . \qquad (10)$$

The experimental values of EV and the recoil free paths R calculated from Eqn. (5) can be used to find the diffusion coefficient D and the specific surface S from the set of equations (10). Thus Strassmann[44], from the observed emanating power due to recoil E_0 and the length of the free path R, determined the specific surfaces for various specimens of barium salts, and Heckter[18] made the same determinations on powdered glass specimens. The use of the emanation method to determine the absolute value of the surface area and the diffusion coefficient for the atoms of the inert gas in the solid is restricted, however, by the inaccuracy of the equations used, as noted above.

Zhabrova, Shibanova (Sinitsyna), Roginskii, and Gordeeva compared the dependence of the specific surface and emanation coefficient on the temperature conditions and degree of dehydration of magnesium, thorium, and zirconium hydroxides[11,50]. The change in the same sense in these two characteristics of a solid (Fig. 3) leads to a linear relationship between them; this may also be true for a number of other metal oxides.

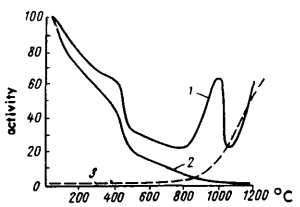


Fig. 2. Typical curves showing the change in emanation as iron hydroxide gel is heated: 1) activity during heating; 2) activity after heating; 3) activity on repeated heating.

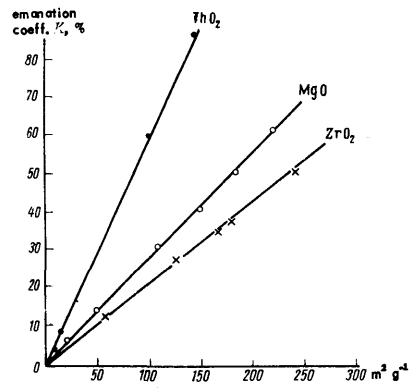


Fig. 3. Dependence of the emanation coefficient with respect to thoron on the specific surface for the oxides of thorium, magnesium, and zirconium.

4. THE USE OF RADIOACTIVE INERT GASES TO STUDY PHASE TRANSITIONS, CHANGES IN CRYSTAL STRUCTURE, AND THE MOBILITY AND DIMENSIONS OF PARTICLES

It can be seen from the work already cited that the emanation method makes it possible to follow changes in crystal structure and phase transitions occurring in salts and oxides when heated to high temperatures. Strassmann[44] observed a sharp increase in the emanation of barium sulphate between 700° and 800°C, when almost quantitative liberation of the emanation takes place in a short time interval. This temperature range corresponds to the Tammann temperature, at which breakdown and sintering of the salt begin. A more detailed study of barium sulphate and carbonate was made by Zaborenko and Babeshkin[32], who recorded the α-activity continuously. They confirmed the breakdown of the barium sulphate lattice in the range 650–800°C, but they also observed an increase in the emanation accompanying the polymorphic transformation of the salt above 1100°C. The emanation method was also used to determine the temperature of the two phase changes for barium carbonate. The enantiotropic transitions in barium carbonate were reported even earlier by Zimens[51,52], who used the emanation method to study the thermal behaviour of the alkaline-earth metals. The heating curves obtained in a current of carbon dioxide for calcium carbonate labelled with ThX showed changes in EV corresponding to the phase change from aragonite to calcite, the subsequent dissociation of the carbonate, and the breakdown of the structure of the calcium oxide formed.

Zaborenko and coworkers[12] showed, for the example of $KCl-CaCl_2$ and $CaO-Fe_2O_3$ (Fig. 4), that it is possible in principle to study equilibrium diagrams by the emanation method. The melting points of the eutectics on the emanation curves were determined from the temperatures of the maximal rates of decrease in emanating power. The observed temperature ranges corresponding to the phase transitions showed good agreement with published data.

In a study of phase changes in quartz, Sizmann and Rupp[53] made use of the absorption of radioactive krypton when the specimen was heated in a current of ^{85}Kr. It was observed that there was a marked increase in absorption of the gas at the point corresponding to the irreversible conversion of β-quartz into β-cristobalite (930° ± 15°C), whereas no such increase was observed for the reversible conversion of α-quartz into β-cristobalite (270°C) or of α-quartz into β-quartz (575°C). This difference was attributed to the difference in the phase transitions: in the first instance, a new crystal lattice was formed; whereas in the second, only rearrangement took place.

As noted above, the emanation method makes it possible to determine the temperature at which breakdown of the crystal lattice of a solid takes place. Schröder and Fricke[54] studied this problem, and also established the influence of preliminary aging of aluminium, iron, titanium, and tin oxides on the Tammann temperature and the shape of the emanation curves. They noted[54] that a sharp increase in the emanating power of the specimen always occurred at the temperature corresponding to the increase in mobility of the crystal lattice. For oxides previously heated at high temperatures, the start of the rising section on the heating curves is indistinct, and generally corresponds to a temperature which is higher than half the absolute melting point of the given oxide. For oxides which have not been subjected beforehand to treatment at high temperatures, the Tammann temperature corresponding to breakdown of the solid can be determined accurately from the inflection or minimum on the emanation curve, above which there is a prolonged increase in the liberation of emanation with rise in temperature (Fig. 5). An exception is aluminium oxide, for which the breakdown of the lattice does not give a sufficiently marked change in emanation; this was attributed to the low degree of ordering of its primary and secondary structures. When the emanation method is used to study processes taking place at high temperatures (1100–1200°C), allowance must be made, in accordance with Anderson's data[55], for the possibility of diffusion of ThX to the surface of the solid; this may lead to an increase in emanation which is not associated with a change in the specimen itself.

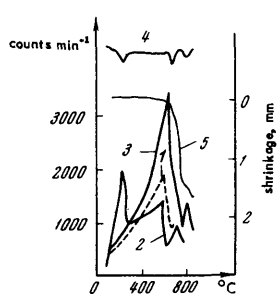


Fig. 4. Heating curves for mixtures of potassium chloride and calcium chloride activated with radiothorium. Emanation polythermals (mole % of $CaCl_2$): 1) 25; 2) 40; 3) 60; 4) differential thermal analysis curve (60); 5) shrinkage curve (60).

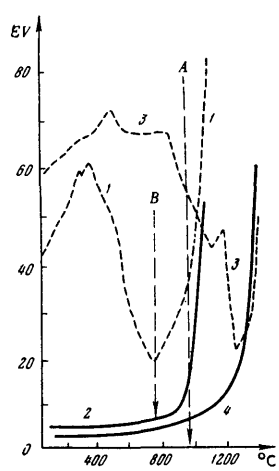


Fig. 5. Emanating power of: 1) γ-FeOOH; 2) α-Fe_2O_3 previously heated at 1000°C; 3) γ-AlOOH; 4) α-Al_2O_3 previously heated at 1000°C. A = 939°C (0.5 × m.p. of Al_2O_3); B = 685°C (0.52 × m.p. of α-Fe_2O_3).

A very interesting series of papers by Gregory and Moorbath[56,57] describe a study of the diffusion of thoron in barium stearate, and also during the dehydration and phase transitions of aluminium oxide. Unlike many other workers, these authors carried out a theoretical treatment of their results, and observed good agreement between experimental and calculated values. On the basis of the theory of emanation put forward by Flügge and Zimens[14,15], Gregory and Moorbath calculated the diffusion coefficient, activation energy, and mean particle size for aluminium oxide heated at various temperatures. From a study of the dependence of the emanating power of α-Al_2O_3 on the partial pressure of oxygen, they concluded[56,57] that a relationship exists between the degree of non-stoichiometry (defectiveness) of the aluminium oxide lattice and the rate of diffusion of thoron. The dependence of the emanating power on the defect nature of and quantity of non-stoichiometric oxygen in nickel oxide and zinc oxide containing added lithium and gallium oxides was studied by Shibanova and Zhabrova[58]. Thus, for example, a marked increase in the emanation (Fig. 6), evidently due to breakdown of the crystal lattice, begins with the original ZnO specimen (curve *1*) close to Tammann temperature (850–900°C). When lithium oxide is added, the increase in the quantity of emanation liberated from zinc oxide with rise in temperature is more clearly defined, and the temperature at which the ions of the crystal lattice begin to become mobile (the Tammann temperature) is lowered (curve *2*). The addition of the oxide of a metal with higher valency, in particular gallium oxide, leads to a marked decrease in the rate at which the emanating power of zinc oxide increases with rise in temperature (curve *3*). The effects observed are reversible, since repeated heating of the zinc oxide specimens containing the added oxides gives analogous results, with a slight decrease in the absolute magnitude of the emanation.

Thus the data obtained by the emanation method agree with the ideas regarding the defect nature of ZnO as due to the presence of interstitial Zn^+ ions, formed on the introduction of Li_2O into zinc oxide[59]. When Ga_2O_3 is added, the defect nature of the ZnO crystal lattice should diminish, leading to a decrease in emanating power. The same investigation showed that increase in the lithium concentration above 1 at.% does not lead to further increase in the emanation. This is probably due to the limited solubility of the added oxide in the zinc oxide being studied.

Yajima and coworkers[60], in a study of the diffusion of ^{133}Xe in natural and synthetic graphite specimens, mixed with uranium oxide and irradiated with neutrons, also observed a relationship between the rate of liberation of the radioactive inert gas and the density of dislocations in the specimens. The use of radiochemical emanation methods for the comparative study of defects produced during the irradiation of solids by various forms of ionising radiation evidently deserves attention. The few papers devoted to this problem, by Jech, Zhabrova, and Shibanova[29,61] and by Mundt and Richter[62], however, are purely qualitative.

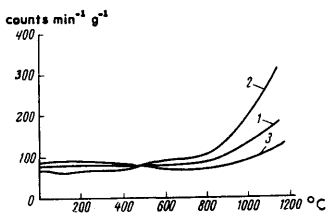


Fig. 6. Temperature dependence of emanating power for:
1) original zinc oxide; and zinc oxide modified with:
2) lithium oxide; 3) gallium oxide.

One of the narrower fields of application of this method is the use of emanation to study the physicochemical properties of metals and alloys[63]. In particular, Werner[64] followed the change in the internal deformation stress of zinc–barium alloys from the liberation of emanation.

5. STUDY OF THE THERMAL DECOMPOSITION AND REACTIONS OF SOLIDS BY EMANATION METHODS

The possibility of using the emanation method to observe phase transitions, the start of breakdown, and increase in the mobility of the atoms of the crystal lattice of solids led, as expected, to the extensive application of this method to study reactions in the solid state; interest in these reactions has increased considerably in the last ten years. This problem has formed the subject of several papers by Schröder and his coworkers[65–69], who studied the changes in the surface and the state of the crystal lattice of individual components of the reaction, and also the formation of chemical compounds, chiefly of the spinel type. They investigated the reactions involved in the preparation of iron–zinc and iron–cadmium spinels[66]. The indicator element was radiothorium, which was introduced into the specimens during the precipitation of highly disperse gels of basic zinc carbonate or zinc hydroxide and iron hydroxide. It was shown that basic zinc carbonate retains radiothorium much more strongly than does zinc hydroxide. The temperature curves for the emanation were used to find the decomposition temperature of basic zinc carbonate (~ 120°C) and the temperature corresponding to the start of appreciable displacement of the ions or atoms of the crystal lattice, ~ 800°C for zinc oxide. Study of the liberation of emanation as a mixture of zinc and iron oxides was heated established that spinel formation takes place in the range 700–800°C, the result being independent of the reactant containing the indicator element. Similarly, the increase in the liberation of emanation was used to determine the temperatures of dissociation, breakdown of the crystal lattice of the components, and spinel formation for mixtures of iron and cadmium oxides.

Later, Schröder[67,68] used the emanation method to study the thermal decomposition of aluminium and beryllium hydroxides. It was again confirmed that the emanation temperature curves obtained directly by heating (the *LT* curve) or by measuring the emanating power of rapidly cooled specimens (the *RT* curve) could be used to detect both chemical changes and allotropic transformations, and also changes in the active states, particularly in the specific surface. The opposite directions followed by the *LT* and *RT* curves at the start of heating (up to 150–160°C) were attributed to a combination of two processes: the liberation of adsorbed water led to an increase in the emanation, and recrystallisation of the hydroxide led to a decrease in the emanation. An interesting result was the detection[68] of an unstable state of beryllium oxide above 600°C, also observed with zinc oxide[65] at a temperature of ~ 25% of the absolute melting point. Hüttig[70]

considered that this temperature corresponded to the start of movement of the ions or atoms on the surface of the solid. The increase in emanation observed with γ-AlOOH, at 1150°C was attributed to the effect described by Hedvall [71], who predicted an increase in the mobility of the ions and the relative maximum of both physical and chemical activities in the transition state, in particular in the transition from γ-Al_2O_3 to α-Al_2O_3.

Schröder and Fricke [69] gave data on the thermal behaviour of a stoichiometric mixture of γ-AlOOH and $Be(OH)_2$, with coprecipitation of both aluminium hydroxide and beryllium hydroxide with radiothorium nitrate. With mechanical mixing of the hydroxides, the emanation curves obtained on heating the mixture differed little from the curves obtained for the starting materials. With jointly precipitated aluminium and beryllium hydroxides, however, the behaviour of the mixture on heating was quite different. When γ-AlOOH and $Be(OH)_2$ were heated separately, a decrease in emanation—due to recrystallisation—was observed at 900° and 800°C respectively whereas with the coprecipitated specimens the liberation of emanation increased sharply above 850°C, corresponding to the formation of beryllium aluminate, and the decrease in EV due to recrystallisation began only at 1150°C. All these results obtained by Schröder and his coworkers were confirmed by X-ray diffraction and analytical data, but unfortunately automatic continuous recording of the α-activity of the emanation liberated was not used, so that rapid processes might have been missed. The method used in the work cited was also used to study the processes involved in the transformation of copper hydroxide [72] $Cu(OH)_2 \rightarrow CuO \rightarrow Cu \rightarrow CuO$; an unambiguous interpretation of both reduction and oxidation processes was made possible by measurement of the quantity of emanation liberated.

The formation of zinc aluminate [73] and magnesium aluminate [74] was studied by the emanation method at a higher methodological level. It was suggested that it is possible to obtain a chemical compound by reaction in the powdered state, even when the lattice parameters of the components are dissimilar, if the mixture is heated sufficiently slowly [73]. In this instance, several intermediate states are observed, when the more mobile component envelops the granules of the passive component and subsequently diffuses into its lattice, with formation of the chemical compound [75]. The theories developed were verified for the example of zinc aluminate formation; the variation in emanation with temperature was recorded both for the individual oxides and for a mixture of zinc oxide and aluminium oxide (Fig. 7). The increase dEV/dt, where EV is the emanating power and t the temperature, is much more marked with zinc oxide than with alumina, owing to the greater mobility of the ions in the zinc oxide lattice. From a comparison of the emanation curves obtained by heating a mixture of inactive zinc oxide and aluminium oxide labelled with radiothorium (curve *6* in Fig. 7) and a mixture of inactive aluminium oxide and zinc oxide containing radiothorium (curve *5*), it was concluded that spinel formation took place above 850°C. [73] An unsatisfactory feature of this work [73] is the lack of data on the specific surfaces of the oxides and their mixtures, although, as shown by Schwab [76], the change in surface area during reactions of powdered components in the solid state may give additional information on the existence of various intermediate stages.

Curves giving the change in emanation when a mixture of barium and calcium carbonates labelled with ThX is heated, and also when Fe_3O_4 labelled with radiothorium is

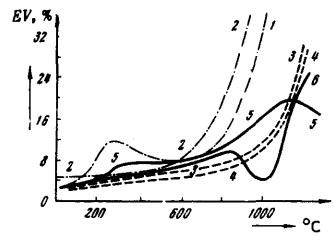


Fig. 7. Temperature dependence of the emanating power of oxides activated with radiothorium:
1) ground ZnO; 2) unground ZnO; 3) ground Al_2O_3; 4) unground Al_2O_3; 5) mixture of activated ZnO with inactive Al_2O_3; 6) mixture of activated Al_2O_3 with inactive ZnO.

heated in an atmosphere of oxygen, were given by Zimens [30], who also described one of the first assemblies for the automatic recording of rapid changes in the quantity of emanation being liberated. The change in the structure of iron oxides was studied in more detail by the emanation method in subsequent work by the same author [14]. The influence of the addition of SiO_2 on the thermal decomposition of iron hydroxide was studied by Götte [77], using the emanation method. Unfortunately, Götte did not give a sufficiently unambiguous interpretation of the results obtained.

Cook [78] used the emanation method to study the processes involved in the dehydration of iron and chromium hydroxides at various temperatures. A most interesting feature is the proposed separation of the emanating power into its components by determining its temperature dependence for specimens subjected to preliminary heating and treatment at a given temperature until a constant value of the emanation was established. This makes possible an indirect determination of the influence of temperature and pretreatment of the specimen on the recoil component of the emanation. Cook [78] correctly pointed out that reliable interpretation of the results is impossible without a detailed study of the changes in the individual components of the emanating power at various temperatures, and allowance for possible errors in the determination of the apparent emanating power; this was also pointed out by Zimens [14].

The decomposition of the hydroxides of zinc, nickel, magnesium, aluminium, zirconium, and thorium over a wide temperature range has been studied simultaneously by the emanation, thermographic, and surface gas labelling methods [11,23]. With all the systems studied, the maximum emanating power coincided almost exactly with the onset temperature of the endothermic effect due to dehydration, determined thermographically. In the zirconium hydroxide–oxide system (Fig. 8), as in the system formed by heating thorium hydroxide, a second emanating power maximum is observed at 400°C. The thermogram for zirconium hydroxide shows a marked exothermic effect at the same temperature. This maximum is due to the crystallisation of previously formed amorphous zirconium dioxide, as has been confirmed by X-ray diffraction studies. The characteristic analogy between thermographic analysis and the emanation method has also been demonstrated in a study of the phase changes in manganese dioxide [79]. The unamibiguous nature of the results obtained

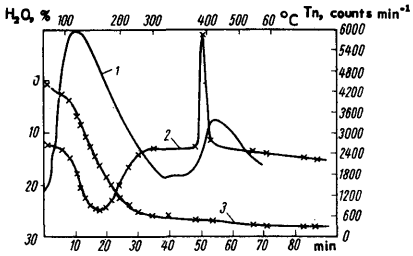


Fig. 8. Curves for zirconium hydroxide: 1) emanation curve; 2) thermogram; 3) change in weight of specimen.

on studying the dehydration of a wide range of metal hydroxides by several methods indicated[79] that the emanation method is applicable also to systems whose oxides do not form true substitutional solid solutions with the added radioactive isotope. The regular distribution of the indicating element was undoubtedly due to the penetration of recoil atoms formed by the disintegration of the radioactive mother element added, and to the high degree of dispersion of the materials studied (5×10^{-6}–5×10^{-5} cm).

Combined investigations of the thermal decomposition of thorium nitrate, thorium oxalate, and barium chloride by emanation, thermogravimetric, and dilatometric methods have been made also by Bussière[13] and by Zaborenko[12]. Particular attention was paid to the methodological aspects of the problem and to the design of assemblies which made possible simultaneous measurement of all the characteristics being studied (the emanation, change in weight of the specimen, and temperature); this eliminated the possibility of errors associated with differences in experimental conditions.

In the study of processes taking place in solids, a knowledge of their kinetics is extremely important. The emanation method is one of the few methods which make it possible to follow changes in structure and surface directly during a topochemical process at a given temperature. The first attempt to use the emanation method to study the kinetics of the formation of calcium silicate from silicon dioxide and calcium oxide was made as early as 1937. Jagitsch[80] published curves giving the time dependence of the liberation of emanation at a given temperature, and put forward a kinetic equation for the change in emanation with time. An unsatisfactory feature of the work was that direct measurement of the emanation was not carried out continuously during the reaction, and only one of the reactants—the silicon dioxide—contained the indicator element. Characteristic "kinetic" curves, giving the change in emanating power with time during dehydration of the hydroxides of magnesium, zinc, thorium, zirconium, and aluminium over the range 100–1000°C, were studied by Roginskii, Zhabrova, and Shibanova (Sinitsyna)[11,81]. The specimens were heated at a definite temperature for a time sufficient to ensure almost complete conversion of the hydroxide into the oxide. The percentage decomposition of the original hydroxide was determined in parallel by weighing at measured time intervals. It was established that the kinetic curves pass through a maximum corresponding in almost all instances to a fairly high percentage decomposition (~ 75–80%). With increase in the temperature of decomposition, the maximum was displaced towards the ordinate axis and at the same time a sharper decrease in activity with increase in the duration of heating was observed. This characteristic form of the kinetic curves giving the time dependence of the emanating power at the temperature of the experiment can be attributed to the combined effects of dehydration, leading to an increase in the specific surface and hence in the emanation of the specimen, and thermal sintering, leading to a decrease in emanation.

6. THE LIBERATION OF RADIOACTIVE INERT GASES DURING CHEMISORPTION AND CATALYTIC PROCESSES ON SOLID SURFACES

Chemisorption and catalytic processes are accompanied by changes in the surface of the catalysts, the formation of surface compounds, blocking of the surface by the reaction products, etc. The use of the emanation method, which is extremely sensitive to all forms of surface and structural changes in solids, to the study of the state of the surface of a catalyst during chemisorption and catalysis is of interest in this connection. Unfortunately, this problem has as yet formed the subject of only a few studies, and these are purely qualitative in character.

Thus Fricke and his coworkers[82,83], in a study of the dependence of the emanating power of magnesium, aluminium, and zinc oxides and γ-Fe_3O_4 on the conditions (temperature, duration of heating, and gaseous medium) of preparation, density, and particle size, observed an increase in the emanation of active magnesium and aluminium oxides as a result of the adsorption of water vapour and carbon dioxide; this was attributed to breakdown of the secondary structure of the oxide. However, these workers did not compare the changes in emanating power with the sorption properties of the magnesium oxide.

Using the method of surface gas labelling described above, Jech[84] established that about half of the radon introduced is liberated from the surface of a platinum catalyst when a hydrogen–oxygen mixture is passed over the catalyst. It was also found that removal of the gas marker takes place chiefly as a result of the reaction of hydrogen with chemisorbed oxygen. An analogous phenomenon is observed in the adsorption of water vapour on platinum at room temperature[84]. It is suggested that this method might be used to detect the location and distribution of active sites on a catalyst surface.

Zhabrova et al.[36] have studied the emanating power of various oxide catalysts (ThO_2, ZrO_2, MgO, and ZnO containing added Na_2O and $ZnSO_4$), labelled with radiothorium, during the chemisorption of the gases and vapours formed in the decomposition of isopropyl alochol. The results obtained show that the physical sorption of gases and vapours of various types has almost no influence on the emanating power of thorium and zirconium oxides. The chemisorption of acetone, water, isopropyl alcohol, and carbon monoxide on the oxides of thorium, zirconium, nickel, and magnesium leads to marked changes in the emanation of these oxides. The original values of the emanating power are generally restored only by regenerating the catalyst in a current of air at 400–500°C. It was suggested that the change in the emanating power of oxide catalysts during chemisorption and catalytic processes may provide a unique criterion indicating the formation of surface chemical compounds and, as can be seen from data on the change in the emanation of modified zinc oxide

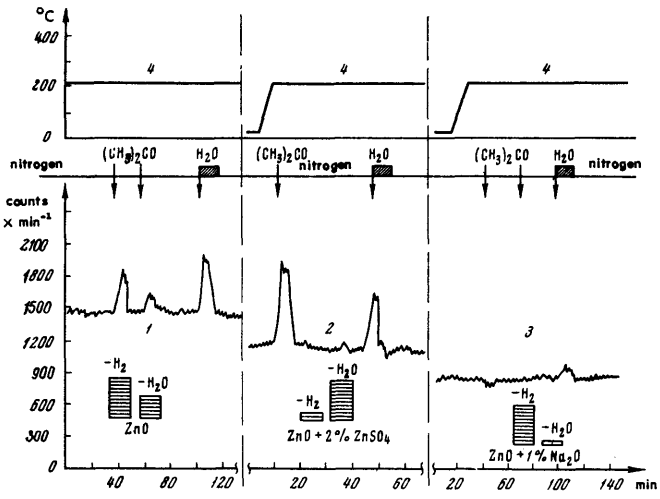


Fig. 9. Emanating power during the chemisorption of acetone and water for:
1) zinc oxide; 2) ZnO + $ZnSO_4$; 3) ZnO + Na^+; 4) temperature of the experiment. The lower diagrams represent schematically the relative proportions of dehydration and dehydrogenation for the various zinc oxide specimens.

specimens during the chemisorption of acetone (Fig. 9), characterising to some extent the strength of the bond formed by the chemisorbed substances with the surface. The results obtained by the emanation method must naturally be subsequently combined with kinetic data on the chemisorption and the characteristics of the catalytic activity of the catalysts studied.

The above results obtained by a large number of workers show the promising possibilities offered by the use of emanation methods in the study of solid-phase topochemical reactions, changes in specific surface, breakdown and thermal sintering, and crystallisation and phase transitions in solids.

It is fairly difficult to obtain radioactive materials with a high specific activity and a minimum concentration of impurities, and also to develop methods of introducing the original radioactive materials, for example in the study of almost insoluble polymers. It is also necessary to make allowance for the characteristic features of each version of the emanation method, described above.

The high sensitivity of the emanation method makes it possible to detect fine differences in the crystal structures of solids, for which X-ray diffraction does not always give sufficient information. At the same time the emanation method is a sensitive analogue of differential thermal analysis, and makes it possible to detect crystallisation and phase changes accompanied by extremely small thermal effects, which are almost undetectable by the latter method.

The method of ion bombardment has recently begun to be used in the study of the mechanism of the diffusion of inert gases in oxides and metals [85-87]. This new approach, making it possible to determine the activation energy of diffusion [86,88] and to study the low-temperature diffusion of radioactive inert gases, which depends on the previous treatment of the surface [87], undoubtedly deserves further development.

It is also of interest to use both the emanation method and the introduction of radioactive inert gases by ion bombardment for the solution of a number of problems related to the state of the active surface of catalysts at various stages in their preparation and application. In most instances, emanation methods must be combined with other methods—sorption, kinetic, X-ray diffraction, thermographic, etc. —and may then give new data in the study of surfaces, structures, and chemical reactions taking place in the solid phase.

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PRIMARY PRODUCTS OF THE RADIOLYSIS OF WATER AND THEIR REACTIVITY

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INTRODUCTION

It is well known that radiolytic transformations in dilute aqueous solutions result from reactions of the solutes with products of the radiolysis of water†. Until recently, research workers considered that these products were the H atom, the OH and HO_2 radicals, molecular hydrogen, and hydrogen peroxide. The latest stage in the development of the radiation chemistry of water and aqueous solutions has been marked by the discovery of yet another primary product of the radiolysis of water—the hydrated electron e^-_{aq}.

In recent years, considerable progress has also been made in the study of the kinetics of radiation reactions in aqueous solutions. The absolute values of the rate constants of many reactions involving intermediate products

† The radiolysis of water and aqueous solutions has been examined in detail by a number of authors [1-4].

of the radiolysis of water have now been determined. It is thus possible to compare their properties, and also (which is particularly important) their reactivities towards various dissolved substances‡.

1. THE FREE-RADICAL THEORY OF THE RADIOLYSIS OF WATER

In 1944 Weiss[5] put forward the hypothesis that the action of ionising radiation on water produces H and OH free radicals. Subsequently, this hypothesis was confirmed in many studies and was developed further.

The free radicals appear as a result of a number of physical and chemical processes, taking place after the passage of the ionising particle through the water. These processes can be characterised briefly by the following time parameters[6]. Transfer of the energy of the ionising radiation to the water takes place in 10^{-16}–10^{-18} s, with the production of excited water molecules, H_2O^* ions, and secondary electrons. The last of these have considerable energy, and ionise and excite more water molecules. Ultimately, with γ-radiation, X-rays, or electron irradiation, individual isolated groups of ionised and excited molecules ("spurs") are formed, where the primary stages of the chemical action of the ionising radiation develop. With heavy charged particles, these spurs lie close to one another, and immediately after their appearance they merge to form a continuous cylindrical column.

After about 10^{-13}–10^{-14} s, dissociation of the positive ion takes place:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH. \qquad (1)$$

Reaction (1) in the gas phase has a rate constant[7] of 5×10^{11} litres mole^{-1} s^{-1}.

Opinions differ regarding the fate of the secondary electron. Most authors, following Lea[8], Gray[9], and Platzman[10-12], consider that the electron, before undergoing thermalisation, moves a considerable distance from its point of origin. At this distance, it is almost uninfluenced by the coulombic field of the mother ion (more accurately, the H_3O^+ ion), so that this electron becomes, as it were, free. It polarises the medium and as a result is "trapped" by the latter, i.e. it becomes hydrated, and in this form takes part in the radiolytic transformations of dissolved substances. The process of "self-capture" of the electron is complete in about 10^{-10}–10^{-11} s. It should be emphasised that the concepts of polarisation "self-capture" of the electron by the medium were first developed by Landau[13] and by Pekar[14] in the physics of solids, where such an electron is called a polaron. This theory was modified and applied to liquids by Davydov[15] and by Deigen[16]. It was extended by Platzman[10-12], with some limitations, to the radiation chemistry of water and aqueous solutions. The suggestion that an important part in the radiolytic transformations of dissolved substances is played by e^-_{aq} was first put forward by Stein[17,18] and by Weiss[19].

Another hypothesis has recently been developed by Magee[20] and by Sworski[21]. At the instant of formation of the H_3O^+ ion [reaction (1)], the dielectric relaxation of the water is not complete, so that this ion is not the ordinary solvated ion. In the opinion of these authors, the electron is attracted to this ion:

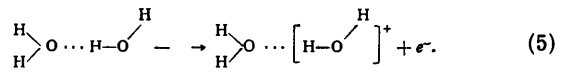
$$H_3O^+ + e^- \rightarrow H_3O. \qquad (2)$$

The H_3O particle may undergo thermal dissociation in two ways:

$$H_3O \rightarrow H + H_2O \qquad (3)$$

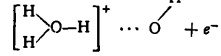
$$H_3O \rightarrow e^-_{aq} + H_3O^+. \qquad (4)$$

According to Sworski[21], the formation of OH and H_3O particles takes place as a result of the ionisation of one of two water molecules joined by a hydrogen bond:

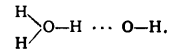


(5)

This is followed by transfer of a proton:



and neutralisation of the charges:



The main difference between these two hypotheses lies in the initial distribution of the e^-_{aq} and OH radicals. According to the first hypothesis, the hydrated electrons are distributed more diffusely than the OH radicals. According to the Magee–Sworski hypothesis, the two types of radicals have identical initial distributions§. It is difficult to give preference to either of these hypotheses. In order to settle this question, it is necessary to carry out accurate diffusion-kinetic calculations¶ of the initial dimensions of the spurs for the OH radicals and reducing-agent radicals, using up-to-date values for the rate constants of the reactions of H atoms, e^-_{aq}, and OH radicals.

Thus about 10^{-10}–10^{-11} s after passage of the ionising particle, the track contains OH radicals, e^-_{aq}, H_3O^+ ions, and excited water molecules. Their concentration is fairly high (~ 0.1–1.0 M), so that, with the track becoming broader as a result of diffusion, they react extremely rapidly with one another:

$$e^-_{aq} + OH \rightarrow OH^- \qquad (7)$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \qquad (8)$$

$$e^-_{aq} + e^-_{aq} + H_2O \rightarrow H_2 + 2OH^- \qquad (9)$$

$$e^-_{aq} + H + H_2O \rightarrow H_2 + OH^- \qquad (10)$$

$$OH + OH \rightarrow H_2O_2 \qquad (11)$$

$$H + H \rightarrow H_2 \qquad (12)$$

$$H + OH \rightarrow H_2O \qquad (13)$$

$$H_3O^+ + OH^- \rightarrow 2H_2O. \qquad (14)$$

‡ Except where otherwise stated, the present review deals with radiolysis under the influence of X-rays, γ-radiation, and fast electrons.

§ Recently, Peers and Cottin[22] have studied the production of H_3O^+ ions on electron collision (energy of the electrons 11–20 eV) in water vapour. They find that these ions are formed chiefly from H_2O^+. Some of the ions, however, appear at a rate which is independent of the field intensity in the ion source. These workers conclude that the precursor of this fraction of the H_3O^+ is "excited water":

$$H_2O^* + H_2O \rightarrow H_3O^+ + (OH + e^-). \qquad (6)$$

It may therefore be assumed that in liquid water some of the hydrated electrons may be produced by the breakdown of H_2O^*.

¶ The problems of diffusion kinetics in the radiolysis of water have been examined in various reviews[23-26].

The above processes have high rate constants (5×10^9–10^{11} litres mole^{-1} s^{-1} [27-52]). Reactions (9)–(12) lead to formation of the so-called molecular products of the radiolysis of water (H_2 and H_2O_2), and reaction (8) leads to the production of H atoms. Kuppermann[53] made appropriate diffusion-kinetic calculations and found that the value of G_H, determined on the assumption that the H atoms are formed in the "spurs" by reaction (8), is close to the experimental value.

The reactions in the tracks take place in an interval 10^{-8}–10^{-10} s after passage of the ionising particle. When the time interval exceeds 10^{-8} s, the "spurs" have become so broad, and the concentration of particles in them has decreased to such an extent, that some of their reactions with dissolved substances in the bulk of the solution become significant.

2. THE HYDRATED ELECTRON

The formation of e^-_{aq} during the radiolysis of water has been proved many times. The proofs can be divided into the following categories.

1. Proof by the method of competing acceptors[54-102]. This method has revealed that the reducing radicals can exist in two forms.

2. Proof using the kinetic salt effect[27,55,103-111]. It is found for a number of reactions that the chief reducing species in the radiolysis of water has a charge of –1.

3. Proof by the pulse radiolysis method[31,42,112-117]. This method has revealed short-lived optical absorption with a maximum at 720 nm for H_2O [31,42,116,117] and 690 nm for D_2O [117] in irradiated liquid water†. This absorption does not appear in acid medium and disappears in the presence of electron acceptors.

4. Proof by electron spin resonance (e.s.r.)[126-127]. Trapped electrons have been identified by this method in alkaline[126-135] and neutral[136,137] vitreous frozen aqueous solutions subjected to the action of radiation at 77°K.

5. Proof by measurement of the electrical conductivity of irradiated water[138-140]. This method has shown, in particular, that the electrical conductivity of water "induced" by radiation disappears in a time interval which is approximately the same as that for the corresponding optical absorption.

Thanks to efforts in many laboratories, the properties of e^-_{aq} have been studied in considerable detail‡. The first point to be noted is that this species is a powerful reducing agent. It reacts with ions of the type M^{2+}, where M represents a metal, to give ions M^+ having an anomalous valency[162-164]. This has been demonstrated for Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, etc.

When the water does not contain e^-_{aq} acceptors, the hydrated electron, at low dose rates, reacts with water with the production of an H atom[31,42,44,115,154,165,166]:

$$e^-_{aq} + H_2O \rightleftarrows H + OH^-. \quad (15)$$

Reaction (15) is slow. According to the latest data[166], $k_{15} = 16$ litres mole^{-1} s^{-1}. The reaction is reversible, and the value of pK for the equilibrium is 9.6.[166] The conversion of the H atom into e^-_{aq} in alkaline medium was demonstrated by Matheson and Rabani[44], who measured the optical density of e^-_{aq} in neutral medium and in a solution of alkali (pH 13) saturated with hydrogen at pressures up to 100 atm, for equal radiation doses per pulse, and found that the optical density of e^-_{aq} is greater by a factor of about 2.2 in the second system than in the first. In alkaline solution reactions (15) (the reverse reaction) and (16) take place:

$$H_2 + OH \rightarrow H + H_2O. \quad (16)$$

Thus $G(e^-_{aq}) = Ge^-_{aq} + G_H + G_{OH} \simeq 2.2Ge^-_{aq}$.

In acid medium, e^-_{aq} is effectively converted into the H atom [reaction (8)]. The rate constant for this reaction is 2×10^{10} litres mole^{-1} s^{-1}.[27-31,42]. This transformation also takes place in the reactions of e^-_{aq} with ions which are proton donors (e.g. $H_2PO_4^-$, HPO_4^{2-}, etc.)[89,154,165].

The reactions of the hydrated electron can be divided into three groups[160]. The first group corresponds to simple addition, e.g.

$$e^-_{aq} + O_2 \rightarrow O_2^- \quad (17)$$

$$e^-_{aq} + C_{10}H_8 \rightarrow C_{10}H_8^-. \quad (18)$$

The second group corresponds to simple reduction, of the type

$$e^-_{aq} + Cu^{2+} \rightarrow Cu^+. \quad (19)$$

The third group corresponds to dissociative addition:

$$e^-_{aq} + ClCH_2COOH \rightarrow [ClCH_2COOH]^- \rightarrow Cl^- + CH_2COOH. \quad (20)$$

The pulse radiolysis method has identified many-short-lived species which are products of the reactions of e^-_{aq} with dissolved substances. The characteristics of the optical spectra of these species are given in Table 1.

The rate constants for the reactions of e^-_{aq} with about 400 compounds have now been determined, chiefly by the pulse radiolysis method. Scheme 1, prepared from published data[27-32,42,44,50,92,106,114,117-153,165,166,171,176-180,183-205] characterises the reactivity of e^-_{aq} with respect to various substances§. Most of these constants have been found from the rate of disappearance of the optical absorption of e^-_{aq} in the presence of the given compound.

On the basis of published data, some general conclusions may be reached regarding the reactivity of this reducing species.

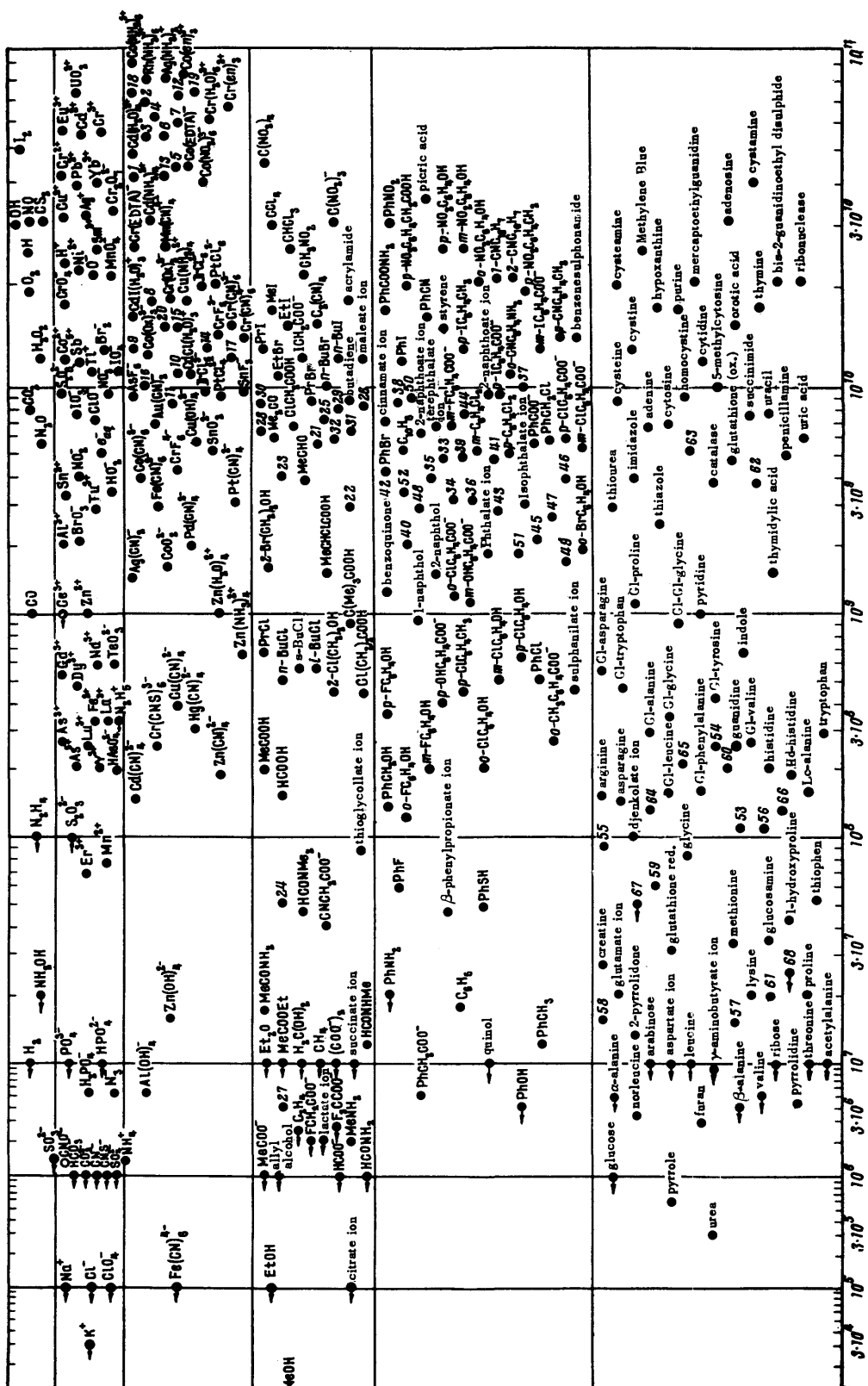
1. The hydrated electron is highly reactive towards molecules which have unpaired electrons, e.g. H, OH, and NO.

2. In the reactions of e^-_{aq} with cations, the rate constants are generally greater the greater the charge and dimensions of the cation.

† An identical absorption band has been observed in the flash photolysis of aqueous solutions of various inorganic ions (Cl^-, Br^-, I^-, CNS^-, $Fe(CN)_6^{4-}$, and OH^-) and organic compounds (phenol, alanine, etc.)[118-123]. In these examples, e^-_{aq} is produced by excitation of the solute by light. Similar phenomena are observed with solutions in ethanol[124,125].

‡ The properties of e^-_{aq} have been examined in a book by Pikaev[4] and in various reviews[141-161].

§ A large number of absolute values of the rate constants for the reactions of e^-_{aq} are given in Pikaev's book[4] and in various reviews[141-143,152,204,205].

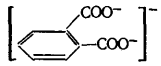
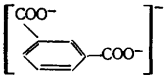
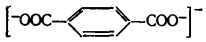
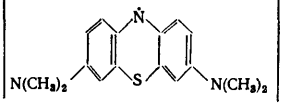


Scheme 1. Rate constants for the reactions of e^-_{aq} in aqueous solution at room temperature:
1) $[CoCl_2en_2]^+$; 2) *cis*-$[Co(CNS)_2en_2]^+$; 3) *trans*-$[Co(CNS)_2en_2]^+$; 4) $[Co(H_2O)(NH_3)_5]^{3+}$; 5) $[Co(H_2O)_4(NH_3)_2]^{3+}$; 6) $[CoCl(NH_3)_5]^{2+}$; 7) $[Co(NH_3)_6$ (teraphthalate)$]^{+*}$; 8) $[CoCl(CN)_5]^{2-}$; 9) $[Co_2N_3(CN)_8]^{4-}$; 10) $[Co(OH)(CN)_5]^{2-}$; 11) $[Co(NO_2)(CN)_5]^{3-}$; 12) $[Cr(CNS)_2en_2]^+$; 13) $[Cr(CNS)_4en_2]^-$; 14) *cis*-$[CrOx_2(H_2O)_2]^-$; 15) *trans*-$[CrOx_2(H_2O)_2]^-$; 16) PbO_2^-; 17) $[PdCl_4]^{2-}$; 18) $[Os(NH_3)_6]^{3+}$; 19) $[Ru(NH_3)_6]^{3+}$; 20) $[Ir(NH_3)_6]^{3+}$; 21) bromopropionate ion; 22) β-bromopropionate ion; 23) $ClCH_2COO^-$; 24) β-phenylpropionate ion; 25) β-iodopropionate ion; 26) CCl_3COO^-; 27) nitrilotriacetate ion; 28) $BrCH_2COO^-$; 29) fumarate ion; 30) methacrylate ion; 31) pyruvate ion; 32) CF_3Cl; 33) *o*-iodobenzoate ion; 34) *o*-hydroxybenzoate ion; 35) *p*-fluorobenzoate ion; 36) *o*-fluorobenzoate ion; 37) *p*-cyanobenzoate ion; 38) *o*-hydroxybenzonitrile; 39) *m*-hydroxybenzonitrile; 40) *p*-hydroxybenzonitrile; 41) *o*-dichlorobenzene; 42) *p*-bromophenol; 43) *o*-bromophenol; 44) *p*-bromobenzoate ion; 45) *p*-aminobenzoate ion; 46) benzenesulphonate ion; 47) *m*-toluate ion; 48) *p*-toluate ion; 49) toluene-*p*-sulphonate ion; 50) α-trichlorotoluene; 51) α-trichlorotoluene; 52) trimesate ion; 53) leucylglycine; 54) leucyl-leucine; 56) phenylalanine; 57) sarcosine; 58) serine; 59) thiobarbiturate ion; 60) tyrosine; 61) acetylglycine; 62) acemosine-5-phosphate**; 63) adenylic acid; 64) alanylalanine; 65) alanylglycine; 66) alanyl-leucine; 67) *d*-sorbitol; 68) *d*-xylose; Me= CH_3; Et = C_2H_5; Pr = C_3H_7; Bu = C_4H_9; Ph = C_6H_5; Gl = glycyl; Hd = histidyl; Lc = leucyl; en = ethylenediamine; EDTA = ethylenediaminetetra-acetate ion; Ox = oxalate; ⟵ = upper limiting value of constant; ⟵• = lower limiting value of constant.

Notes. (1) In those instances where the published values of the constants were given for various pH-values, the Scheme gives the value at pH 6 ÷ 8. (2) The rate constants for the reactions of e^-_{aq} with H_2O and D_2O are 16 and 200 litres mole^{-1} s^{-1} respectively.

* Possibly $[Co(teraphthalate)(NH_3)_5]^+$ (Ed. of Translation).
** This entry may be a misprint in the Russian, and the compound referred to may be adenosine-5'-phosphate (Ed.of Translation).

TABLE 1. Characteristics of the optical spectra of the species produced in the reactions of e^-_{aq} with dissolved substances.

Substance	Reaction product	λ_{max}, nm	ϵ at λ_{max}, litres mole^{-1}	Ref.
O_2	O_2^-	240—250	$9.8\cdot10^3$ at 253.7 nm	12,167,168
I_2	I_2^-	370—390	—	165
CO_2	CO_2^-	250	$2.4\cdot10^3$	169
Ag^+	Ag^0	313	$2.3\cdot10^4$	106,170,171
Tl^+	Tl^0	~400	—	172
Mn^{2+}	Mn^+	300	—	106,162
Co^{2+}	Co^+	300	—	106,162
Ni^{2+}	Ni^+	300	$2.1\cdot10^3$ at 313 nm	106,173
Zn^{2+}	Zn^+	300	$5.2\cdot10^3$ at 313 nm	106,162
Cd^{2+}	Cd^+	300	$7.5\cdot10^3$ at 313 nm	106,162
Pb^{2+}	Pb^+	300	—	162
Eu^{3+}	Eu^{2+}	320, 250	—	174
CrO_4^{3-}	Cr(V)	365	—	106
$PtCl_4^{2-}$	Pt(I)	450, 300	—	106
$S_2O_8^{2-}$	SO_4^-	444	—	175
CH_3I	I^-	220	—	176
$(CH_3)_2CO$	$(CH_3)_2COH$*	absorption in the range 200—300 nm	—	177
CH_3NO_2	$CH_3NO_2^-$	270	$2.8\cdot10^3$	178
$C(NO_2)_4$	$C(NO_2)_3^-$	350	$1.48\cdot10^4$	92,179
		380	—	180
$C_6H_5COO^-$	$[C_6H_5COO^-]^-$	444, 322	—	181
Phthalate		310	—	177
Isophthalate		430, 330	—	177
Terephthalate		520, 360	—	177
Benzophenone	$(C_6H_5)_2CO^-$	610	—	182
Methylene Blue		420	$1.04\cdot10^4$	183

* Produced with the intermediate formation of $(CH_3)_2CO^-$.

TABLE 2.

Property of e^-_{aq} *	Numerical value	Ref.
Charge	—1	27,55,103—111
λ_{max} in H_2O (25°C)	720 nm	31,42,116,117
λ_{max} in D_2O (25°C)	690 nm	117
$\epsilon^{H_2O}_{720}$	15 800 litres mole^{-1} cm^{-1}	179
E^0	$\leqslant$2.58 V	166,206—208
Hydration energy	1.75—1.87 eV	166,207,208
Free energy of formation ΔG°_f	—37.5 kcal mole^{-1}	207
Entropy of hydration ΔS°_{hydr}	—1.9 cal mole^{-1} deg^{-1}	207
Entropy in 1 M ideal soln. S°	3.1 cal mole^{-1} deg^{-1}	207
Diffusion coeff.	$4.7\cdot10^{-5}$ cm^2 s^{-1}	139
Mean radius of distribution of charge	2.5—3.4 Å	207,209,210
k ($e^-_{aq} + H_2O$)	16 litres mole^{-1} s^{-1}	166
$\tau_{1/2}$	$\geqslant7.8\cdot10^{-4}$ s	166
pK ($e^-_{aq} + H_2O \rightleftarrows H + OH^-$)	9.6	166
$G_{e^-_{aq}}$ (pH 7.0)	2.6 (±10%)	179
$G_{e^-_{aq}}$ (pH 13.0)	3.6—3.8	55,91,117

* In this and subsequent tables, ϵ, E^0, and $\tau_{1/2}$ denote respectively the molecular extinction coefficient, standard redox potential, and half-life.

3. The reactivity of e^-_{aq} with respect to anions decreases with increase in the charge on the anion. The hydrated electron reacts slowly with the anions of elements in higher oxidation states, and with anions whose central atom has no vacant orbital accessible to the electron.

4. The reactivity of complex compounds towards e^-_{aq} is parallel to their reactivity in outer-sphere redox processes. Here, however, the hydrated electron is a much more powerful reductant than most ordinary chemical reducing agents.

5. The hydrated electron reacts with organic substances as the strongest nucleophilic reagent, and it generally reacts at the positive centre of the molecule.

The chief properties of the hydrated electron are summarised in Table 2.

The question of the magnitude of $G_{e^-_{aq}}$ has been the subject of lively discussion for a number of years. For a neutral medium, various authors[55,60,72—75,77,81,82,89—91,97,101,107,110,211—236] have given values for the yield of e^-_{aq} of 2.2–2.9. These contradictory values are evidently due to the fact that the yields were not determined under comparable conditions. This might have led to differences in the values of $G_{e^-_{aq}}$ as a result of the suppression of reaction (7) in the spurs to different extents[217,237], or to differences in the contribution made by "excited water" to the reaction with the acceptor[54,55,107,108,218], depending on the concentration of the latter and its reactivity. Moreover, it is not excluded that oxygen atoms, which, as postulated by Allen[238], may be produced as a primary product of the radiolysis of water, may react with some substances and be inactive towards others¶. It has recently been found by the pulse radiolysis method that in neutral medium $G_{e^-_{aq}} = 2.6$ (accuracy ±10%)[179]. In these examples the yield was found directly from the measured values of $\epsilon G_{e^-_{aq}}$ and ϵ.

Published data[55,107,108,221,224,233,234,240—250] on the magnitude of $G_{e^-_{aq}}$ in alkaline medium are also contradictory. Most authors consider, however, that the yield of e^-_{aq} is greater in alkaline than in neutral medium. This is confirmed by direct measurement of $G_{e^-_{aq}}$ at various pH-values, using the pulse radiolysis method[117,251]. There may be several reasons for the increase in $G_{e^-_{aq}}$ in alkaline medium. Firstly, the H atom (if it is formed as a primary product of the radiolysis of water) is converted in alkaline solution into e^-_{aq}. This process alone, however, can increase $G_{e^-_{aq}}$ to only 3.2–3.4. Secondly, it is possible that hydrated electrons are produced by the reaction of OH^- ions with excited water molecules or radical pairs (H + OH) in the cell[54,55]:

$$OH^- + H_2O^* \rightarrow e^-_{aq} + OH + H_2O \quad (21)$$

$$OH^- + (H + OH) \rightarrow e^-_{aq} + OH + H_2O. \quad (22)$$

Thirdly, $G_{e^-_{aq}}$ may increase as a result of the partial suppression of reaction (7) in the spurs by OH^- ions[224]. Fourthly, it is not excluded that $G_{e^-_{aq}}$ under these conditions may increase partly as a result of the excitation of

¶ The problem of the value of $G_{e^-_{aq}}$ in various media has been discussed in detail by Haïssinsky[239].

OH^- ions by radiation, followed by breakdown of the $(OH^-)^*$ formed:

$$(OH^-)^* \rightarrow OH + e^-_{aq}. \quad (23)$$

In the theory of the self-capture of an electron by a polar medium, use is often made of a model in which the solvent is regarded as a continuous dielectric medium, characterised by macroscopic properties (static and optical dielectric constants, D_{st} and D_{opt}). The additional electron interacts with the polarisation field of the medium. The equation for the energy of bonding of the electron to the medium contains the term $1/D_{opt} - 1/D_{st}$. Since D_{opt} is generally close to unity, capture of the electron by the medium requires that $D_{st} \gg 1$. Calculations based on this model can be made in two ways—(1) by using the electronic-adiabatic theory, and (2) by using the self-consistent field theory—in the first of which it is assumed that the mean velocity of an electron which is weakly bound to the medium is low compared with the velocity of the valency and inner electrons of the solvent molecules. This method has been used by Weiss [61,252], who finds that the mean radius of e^-_{aq} is about 5 Å. A sphere with this radius can contain ~ 10 water molecules. The second theory considers the influence of the mean charge distribution of the additional electron on the electrons of the medium. Jortner [210] considers that this theory is more applicable than the first theory to this problem. The chief results of his calculations are as follows: (1) the radius R_0 of the cavity containing the electron is much smaller for water than for ammonia (it is possible that for water $R_0 = 0$); (2) the mean radius of the distribution of the charge of the electron in the energy ground state is 2.5–3.0 Å; and (3) the optical absorption maximum of e^-_{aq} is due to a $1s \rightarrow 2p$ transition. Since according to the Franck–Condon principle the water molecules retain their orientation during the transition, the excited $2p$-state is not an equilibrium state, and λ_{max} for e^-_{aq} corresponds almost exactly to the hydration energy of this radiolysis product (720 nm = 1.72 eV).

A number of experimental data, however, provide evidence in support of the so-called "cavity" theory [185,253-259], which has often been used to explain the characteristic features of the optical absorption spectra of halide ions in solution [253-258]. According to this theory, the halide ion (in our case e^-_{aq}) is present in a spherical "cavity" (i.e. in a certain volume accessible to the ion in solution), whose radius depends on the nature of the ion and the solvent. The absorption maximum is determined chiefly by the energy required to remove the ion from the cavity into the bulk of the solvent. Contraction of the cavity leads to displacement of λ_{max} towards shorter wavelengths. Decrease in the dimensions of the cavity takes place with fall in temperature and with the addition, to the solution, of anions which bind firmly the protons of water molecules. The optical absorption maximum of e^-_{aq} for concentrated electrolyte solutions is displaced towards shorter wavelengths compared with pure water [185]. Decrease in temperature also displaces λ_{max} for this species towards shorter wavelengths [160]; this effect is observed not only for water, but also for alcohols [260]. Similar relationships are observed in the radiolysis of vitreous aqueous solutions at 77°K. [137,261]

Natori and Watanabe [262] have recently developed a structural theory for e^-_{aq}. On the assumption that the electron is trapped in a quasi-tetrahedron of the icelike structure of water and interacts with the nearest four oxygen atoms and eight hydrogen atoms, they calculated the energy of the optical transition at the absorption maximum and the oscillator strength as 0.8 and 0.26 eV respectively (compared with experimental values of 1.72 and 0.6–0.7 eV).

3. THE HYDROGEN ATOM

In 1954 Livingston and his coworkers [263,264], using the e.s.r. method, detected the formation of H atoms in the radiolysis of aqueous solutions of the acids $HClO_4$, H_2SO_4, and H_3PO_4 at 77°K. Later the production of H atoms in frozen aqueous solutions of acids was observed by many workers [265-277]. The spectrum of atomic hydrogen consists of a doublet with a splitting of 500 oersteds and a g-factor close to that of the free electron. The spectrum of the D atom for a solution of an acid in D_2O consists of a triplet with a separation between the components of ~ 78 oersteds. The yield of H atoms depends on the nature of the anion and the concentration of the acid, and also on the state (crystalline or vitreous) in which the frozen solution is irradiated.

Atomic hydrogen is not detected in pure ice irradiated at 77°K. Its spectrum has been recorded at 4.2°K. [273-276] The initial yield of H atoms amounts in this instance to 0.5–0.9 [273,274]. Rexroad and Gordy [275] consider that the H atoms in ice irradiated at 4.2°K are produced as a result of the capture of electrons ejected from water molecules by H_3O^+ ions present in the matrix. The probability of such capture is obviously increased considerably in acid solutions. This probably explains the increase in the yield of H atoms in frozen solutions of inorganic acids, to 2.0–2.2 in perchloric acid solution at 77°K. [270,277]

The e.s.r. spectrum of H atoms has also been observed in solutions of alkalis and various inorganic salts, irradiated at 77°K. [126,127,129,137,272] In this instance, however, the yield of H is low; it is higher in crystalline alkaline ice than in the vitreous material [129].

At present there is no direct proof of the formation of H atoms in the radiolysis of liquid aqueous solutions. There is only indirect evidence for the production of this species. It has been shown [62-65] that the kinetic characteristics of the reducing species in the radiolysis of acid solutions are identical to those of atomic hydrogen prepared by non-radiative methods.

The part played by H atoms is most significant in the radiolysis of acid solutions. This is due to the fact that, since k_8 is high, e^-_{aq} is converted into H even in dilute acid solutions.

In neutral medium the greater part of the reducing radicals consist of hydrated electrons. The yield of H atoms is 0.5–0.6. This value has been found for G_H by many workers [82,83,86,88,90,97,100,213,278].

When neutral solutions do not contain acceptors of hydrated electrons, the latter, at low dose rates, are transformed by reaction (15) into H atoms, which can evidently take part in corresponding processes. This phenomenon is observed, for example, in neutral solutions of methanol. In this system $G(H_2)$ is almost equal [213] to the sum $G_{H_2} + G_H + Ge^-_{aq}$.

According to Baxendale [279] the reactions of H atoms can be divided into three main groups. The first group corresponds to simple reduction, e.g.

$$H + Cu^{2+} \rightarrow H^+ + Cu^+. \quad (24)$$

The second group comprises the addition of H to unsaturated bonds, e.g.

$$C_6H_6 + H \rightarrow C_6H_7. \quad (25)$$

The third group involves the detachment of H with the formation of H_2. Reactions of this group are extremely characteristic of saturated organic compounds, e.g.

$$CH_3OH + H \rightarrow CH_2OH + H_2. \quad (26)$$

The H atom is characterised by strong reducing properties. Its reactivity is indicated in Table 3, which includes data obtained using pulse radiation. The H atom is generally a weaker reducing agent than e^-_{aq}. This is true for the reactions with NO_3^-, NO_2^-, H_2O_2, N_2O, Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, etc.[56,62,64,66,94,95,146,212,278,285-390] The reactivities of H and e^-_{aq} towards O_2 and OH are almost identical. These reactions involve simple addition of H and e^-_{aq}. The H atom is more reactive than e^-_{aq} towards certain organic compounds, e.g. alcohols. The redox potential of H is 2.1 V.[208]

The rate constants for the reactions of H atoms in aqueous solution are greater (by not more than one order of magnitude) than the constants for the analogous gas-phase reactions. This is in accordance with the theory of chemical kinetics[301].

Hydrogen atoms and e^-_{aq} often give the same reaction products. There is one characteristic property of H atoms, however, by means of which they can be distinguished on the basis of an analysis of the final products. Unlike e^-_{aq}, they exhibit a dehydrogenating action in reactions with saturated organic compounds.

The yield of H atoms is 3.65[1] in acid medium (pH < 2) and 0.5–0.6 in neutral medium[238]. In alkaline medium this species is effectively transformed into e^-_{aq} [reverse reaction (15)].

In 1950 Weiss[302] postulated the formation of H_2^+ radical-ions in acid medium:

$$H + H^+ \rightarrow H_2^+. \quad (27)$$

Later various characteristic features of the radiolysis of acid solutions were also attributed to the production of this radical-ion[71,72]. As shown subsequently, however, the rate constant for reaction (27) is comparatively low, 10^2–2.6×10^3 litres mole^{-1} s^{-1}.[37,296] It has been shown[303] that $G(Fe^{3+})$ in aqueous Fe^{2+} solutions is independent of the acid concentration, indicating that H_2^+ plays little part, even in strongly acid solutions. According to certain authors[62,303,304], the oxidation of Fe^{2+} by atomic hydrogen involves the intermediate formation of hydride complexes:

$$Fe^{3+} + H \rightleftarrows FeH^{3+} \quad (28)$$

$$FeH^{3+} + H^+ \rightarrow Fe^{3+} + H_2. \quad (29)$$

The H_2^+ radical-ion apparently does not oxidise methanol in sulphuric-acid solutions[305].

There are two hypotheses regarding the mechanism of formation of H atoms as a primary product of the radiolysis of water. According to the first, these particles are produced by reaction (8), taking place in the spurs[53,79,80,306]. The second hypothesis[76-78,307-309] suggests that H atoms are produced from highly excited water molecules. According to Anbar and Meyerstein[308] substances which are efficient excitation-quenching agents (in particular ions of variable valency) can apparently react directly with the possible precursors—H_2O^* molecules—of the H atoms. These authors regard[309] the second hypothesis as confirmed by the results of a study of H/D isotope effects in the radiolysis of water. They find[309] that the isotope effect in the formation of H atoms is much greater in acid medium than in neutral medium. At present, however, there are no direct experimental data in support of either hypothesis.

TABLE 3. Rate constants for the reactions of H atoms with dissolved substances at 20–25°C.

Solute	k, litres mole^{-1} s^{-1}	Ref.	Solute	k, litres mole^{-1} s^{-1}	Ref.
Fe^{2+}	$2 \cdot 10^7$	35	HO_2	$2 \cdot 10^{10}$	147
Fe^{3+}	$9 \cdot 10^7$	37	H_2O_2	$(0.9–1.6) \cdot 10^8$	34, 36, 37
Ag^+	$1.15 \cdot 10^{10}$	171	e^-_{aq}	$2.5 \cdot 10^{10}$	28, 44
H	$1.0–1.5 \cdot 10^{10}$	34–46	MnO_4^-	$2.36 \cdot 10^{10}$	283
O_2	$0.53–2.6 \cdot 10^{10}$	33, 34, 37, 45, 280	CH_3OH	$1.6 \cdot 10^9$	171
OH	$0.7–4.5 \cdot 10^{10}$	33, 34, 45, 51	CH_2OH	10^{10}	283
Br_2	$\sim 10^{10}$	281	$C(NO_2)_4$	$(0.55–2.6) \cdot 10^9$	92, 179
OH^-	$(1.8–2.3) \cdot 10^7$	44, 282	$H_2^+ (+H_2^+)^*$	$< 5 \cdot 10^6$	284

* Rate constant for the recombination of H_2^+ radical-ions.

4. THE OH RADICAL

The formation of OH radicals by the action of radiation on water has been observed repeatedly. Dainton and Collinson[310], in a study of the radiation polymerisation of acrylonitrile in water, observed in the infrared absorption spectrum of the polymer a broad band due to OH groups. A large number of products of the reactions of OH radicals with dissolved substances have now been identified by the pulse radiolysis method. A list of these products and some characteristics of their optical spectra are given in Table 4.

Recently, Hart, Matheson, et al.[51], using the pulse radiolysis method, have recorded the optical absorption spectrum of the OH radical in irradiated liquid water. It is found that λ_{max} for this radical lies at $\leqslant$ 230 nm.

One of the most important pieces of evidence for the formation of OH radicals in the radiolysis of water is provided by data obtained from the e.s.r. spectra of irradiated ice. The e.s.r. spectrum of OH radicals radicals in ice irradiated at 77°K was first observed by Matheson and Smaller[265,267]. The e.s.r. spectrum due to OH radicals (in H_2O) and OD radicals (in D_2O) has since been observed by many workers[126,127,137,271-277,328-338]. The e.s.r. spectrum of the OH radical consists of a doublet with a separation of ~ 40 oersteds between the components and a g-factor of 2.01, and that of the OD radical consists of a triplet with a separation of ~ 6 oersteds between the components.

The chief source of OH radicals is H_2O^+ ions (reaction 1). Weiss[252] suggested that H_2O^+ (or, in his terminology, the positive polaron) in liquid water has a lifetime which is sufficient to enable it to take part directly in the radiolytic transformation of various substances. Later, Weiss and Moorthy[339,340] have reported that they were able to record the e.s.r. signal of this ion in a study of the radiolysis of frozen solutions of various acids. Hummel and Allen[341] found, however, that the ionic strength does not influence the rate of the reaction between the oxidising

TABLE 4. Characteristics of the optical spectra of short-lived species which are products of the reactions of OH and O^- radicals with dissolved substances.

Solute	Reaction product	λ_{max}, nm	ϵ at λ_{max}, litres mole^{-1} cm^{-1}	Ref.
O_2 (alkaline medium)	O_3^-	430	$1.9\cdot10^3$	52, 167, 168, 311—313
	NO_2	400	—	314
NO_2^-	CNS	500	$7.1\cdot10^3$	49, 52, 168, 313—316
CNS^-	Cl_2^-	340	$1.25\cdot10^4$	317
Cl^-	Br_2^-	360	$9.6\cdot10^3$	189, 281, 318, 319
Br^-	I_2^-	370—390	—	47, 117, 314, 315
I^-	AsO_2	335	—	314, 315
AsO_2^-	CO_3^-	600	$(1.9—2.9)\cdot10^3$	169, 311, 315, 320
CO_3^{2-}	SiO_3^-	625	—	314, 315
SiO_3^{2-}	SeO_3^-	435	$1.34\cdot10^3$	314, 315
SeO_3^{2-}	TeO_3^-	350	$3.5\cdot10^3$	314, 315
TeO_3^{2-}	$S_2O_3^-$	375	$1.72\cdot10^3$	314, 315
$S_2O_3^{2-}$	HSO_3^{2-}	730	—	314
SO_3^{2-}	HSO_4 (or SO_4^-)	450	$\sim10^3$	321, 322
SO_4^{2-}	Ag^{2+}	270	—	171
Ag^+	Cu^{III}	300 (pH 7) or 265(pH 2)	$1.1\cdot10^3$ for Cu^{2+} and $5.7\cdot10^3$ for $CuOH^{2+}$	106, 323
Cu^{2+}	Mn^{III}	~450	$8.3\cdot10^3$	170
Mn^{2+}	Tl^{2+}	260	—	182
Tl^+	Fe^{IV}	345	$6\cdot10^3$	324
Fe^{2+}	CH_3CHOH	266, 257, 247	$(2.3—2.4)\cdot10^3$ at 296.7 nm	30, 325
C_2H_5OH	$(CH_3)_2COH$	absorption in the range 200—300 nm	—	177
$(CH_3)_2CHOH$				
$HCOO^-$ or CO_2	CO_2^- (COOH)	250	$2.4\cdot10^3$	169
$(NH_2)_2C=S$	$NH_2\diagdown C=S$ / NH	400	—	194
	or $NH_2\diagdown C—S$ // NH			
C_6H_6	C_6H_5OH	313	$3.5\cdot10^3$	326, 327
C_6H_5Cl	OHC_6H_5Cl	324	—	326
C_6H_5Br	OHC_6H_5Br	326	—	326
C_6H_5OH	OHC_6H_5OH	320	—	326
$C_6H_5CH_3$	$OHC_6H_5CH_3$	317	—	326
C_6H_5COOH	OHC_6H_5COOH	350	—	327
$C_6H_5COO^-$ (alkaline medium)	(O^-) $C_6H_5COO^-$	328	—	181

species in the radiolysis of water and bromide ion. Hochanadel[298] found that in the pH range 2–7 the oxidising species in the radiolysis and the OH radical obtained photochemically have the same reactivity towards hydrogen and hydrogen peroxide. From this it follows that the species being considered is not charged. Moreover, the e.s.r. signal observed by Weiss and Moorthy[339,340] has later been shown[137,277] to be due most probably to the OH radical. Nevertheless, it is not excluded that H_2O^+ ions may take part in radiolytic transformations in strongly acidic or highly concentrated solutions, when the reactions of the substances with this species may take place at a greater rate than reaction (1).

The OH radical is a strong one-electron oxidant. On reaction with a solute it oxidises one equivalent of the latter. It can sometimes act as a reducing agent, e.g. in the radiolysis of potassium permanganate solutions[342].

The most characteristic reactions of OH radicals can be divided into three groups. The first group corresponds to ordinary oxidation, e.g.

$$Ce^{3+} + OH \rightarrow Ce^{4+} + OH^-. \qquad (30)$$

The second group comprises the addition of OH to unsaturated bonds. The third group involves the abstraction of H with the formation of H_2O.

In alkaline medium the OH radical dissociates[343]:

$$OH \rightleftarrows O^- + H^+. \qquad (31)$$

The value of pK for this dissociation[39] is 11.9 ± 0.2. Like the OH radical, the O^- radical-ion absorbs in the wavelength range below 300 nm.[39] The ozonide ion O_3^- has been observed during the pulse radiolysis of alkaline solutions of oxygen[167,311] (see Table 4). This ion may be formed by the reaction

$$O^- + O_2 \rightarrow O_3^- \qquad (32)$$

which provides evidence for the existence of O^- in alkaline medium. The dissociation of the OH radical according to Eqn. (31) is also confirmed by measurements of the e.s.r. spectra of irradiated frozen alkaline solutions[126–135,344].

The O^- radical-ion is a weaker oxidising agent than the OH radical. In alkaline medium the yields of a number of oxidation processes—$G(AsO_4^{3-})$ for the oxidation of arsenite[345,346], $G(CO_2)$ for the radiolysis of oxalic acid solutions[347–351], $G(I_2)$ for the radiolysis[221] and photolysis[296] of KI solutions in the presence of N_2O, etc. —show a decrease. On the other hand, there is an increase in the yields for reductions, when the product undergoes reconversion into the starting material as a result of reaction with OH. For example, $G(NO_2^-)$ for $NaNO_3$ solutions increases sharply in alkaline medium[91]. Sometimes it is even necessary to assume that the O^- radical-ion has a reducing action[221,296].

Scheme 2, which indicates the reactivities of OH and O^- radicals, uses data[30–34,36,38,39,44,47,49,51,52,117,147,167–170,177,179,181,182,189,194,200,202,311–327,352–354] obtained in studies in which the reaction rate constants for these radicals were determined by means of pulsed radiation. In addition, a large number of relative rate constants for the reactions of OH and O^- have been determined by the method of competing acceptors[38,205,238,293,341,355–369].

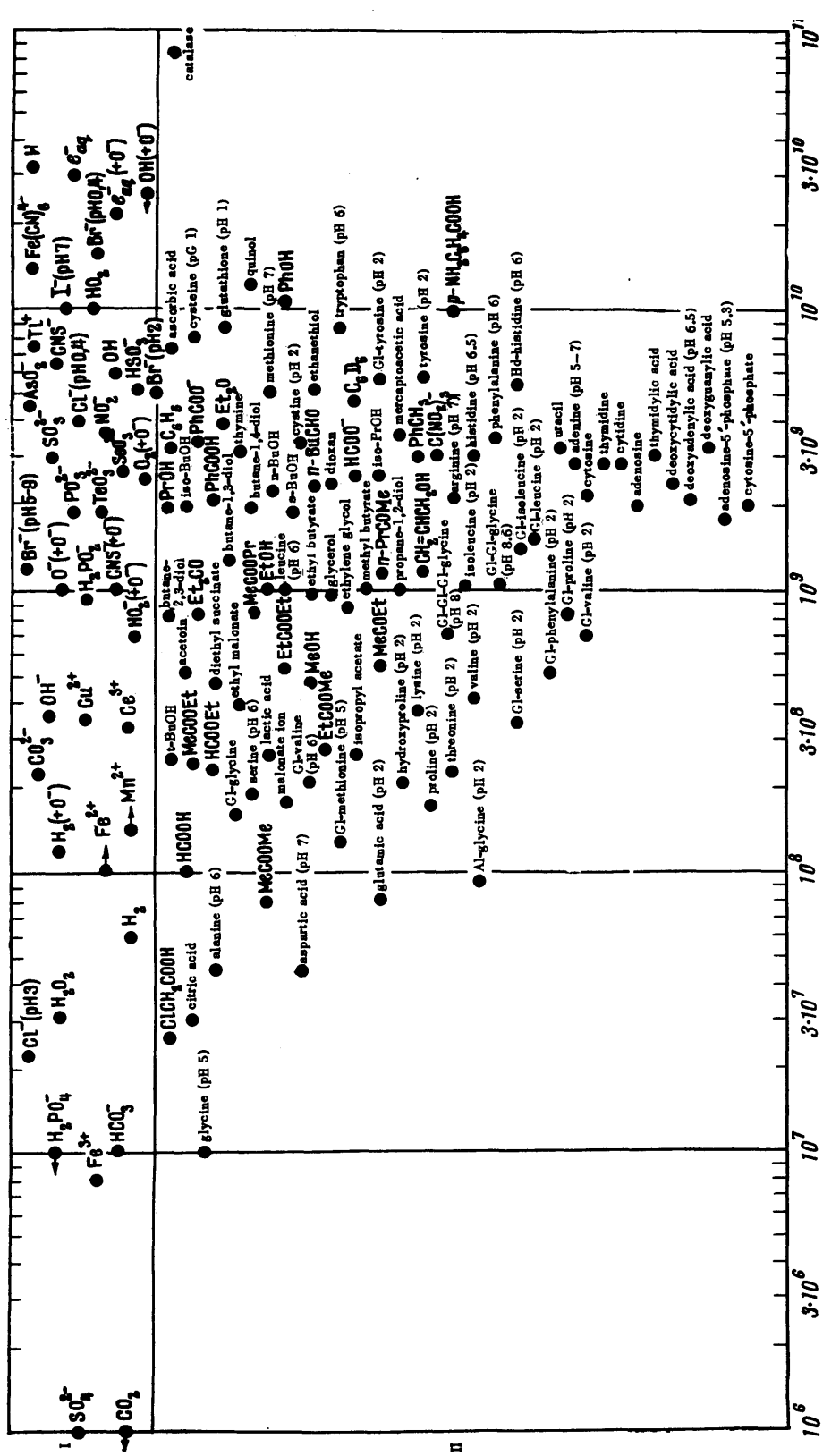
An important feature of the kinetics of reactions involving OH radicals is that the rate constants for reactions of type (13) have much larger values in aqueous solution than in the gaseous phase. Thus $k_{OH + H_2}$ for the gaseous phase is[370,371] about 10^4 litres mole^{-1} s^{-1}; for aqueous solutions, this constant has the value[38] $(4–6)\times10^7$ litres mole^{-1} s^{-1}. There are as yet, however, insufficient experimental data for a rigorous explanation of this effect.

The yields of OH radicals are greater in acid and alkaline media than in neutral medium. Since the processes of

TABLE 5.

Property of OH radicals	Numerical value	Ref.
λ_{max} H_2O (25 °C)	230 nm	51
$\epsilon_{260}^{H_2O}$	370 litres mole^{-1} cm^{-1}	51
E^0 (pH 0)	—2.1 V	372
E^0 (pH 14)	—1.25 V	372
Hydration energy	0.26 eV	372
Diffusion coeff.	$\geqslant2.3\cdot10^{-5}$ cm^2 s^{-1}	202
pK $(OH+OH^-\rightleftarrows O^- + H_2O)$	11.9	39
G_{OH} (pH 0)	2.95	1
G_{OH} (pH 7)	2.6 (±10%) *	
G_{O^-} (pH 13)	3.0—3.1	54, 55, 79

* Mean value from results given in a large number of papers.



Scheme 2. Rate constants for the reactions of OH and O$^-$ radicals in aqueous solution at room temperature. The constants for O$^-$ are denoted (+O$^-$); Al = alanyl; the other symbols are the same as those used in Scheme 1.

OH and e^-_{aq} formation are interrelated, the reasons for the increase in G_{OH} in alkaline medium are for the most part the same as those for the increase in Ge^-_{aq}.

The chief properties of OH radicals in water are summarised in Table 5.

5. THE HO_2 RADICAL

A study of the radiolysis of the Fe^{2+}–Cu^{2+} system by Hart in 1956 showed[373-375] that the perhydroxyl radical HO_2 is formed as a primary product. It is produced in the spurs as a result of reaction between H_2O_2 and OH. The yield of HO_2 for $^{60}Co\gamma$-radiation is extremely low (~ 0.02)[373]. For heavy particles, however, G_{HO_2} is much greater. For ^{210}Po α-particles, $G_{HO_2} = 0.23$.

The HO_2 radical is formed very efficiently in solutions containing oxygen, by reaction between O_2 and H or e^-_{aq}. Since k_{H+O_2} and $ke^-_{aq}+O_2$ have extremely high values, it may be concluded that the HO_2 radical plays an important part in these solutions.

Formation of the perhydroxyl radical has been demonstrated by many methods. Schmidt[377,378] observed an increase in electrical conductivity due to the presence of O_2^-—a product of the dissociation of HO_2—in irradiated water containing oxygen. The pulse radiolysis method has been used[167,177,311,313] to record the optical absorption spectra of HO_2 and O_2^- radicals. The absorption maximum of the HO_2 radical lies at 230 nm, and that of the O_2^- radical-ion at 240 nm. Proof of the formation of HO_2 radicals was also obtained in a study of the e.s.r. spectra of irradiated frozen water and various aqueous solutions[126,127,328,329,333].

The HO_2 radical is amphoteric. In neutral and alkaline media it dissociates according to the equation

$$HO_2 \rightleftarrows H^+ + O_2^-. \qquad (33)$$

The pK value for this dissociation is 4.4–4.5.[167,179,379] According to Bielski and Allen[380], the perhydroxyl radical is present in strongly acidic medium in the form $H_2O_2^+$:

$$HO_2 + H^+ \leftrightharpoons H_2O_2^+ \qquad (34)$$

the pK value for this equilibrium being 1.0 ± 0.4.[380]

The perhydroxyl radical may act as either an oxidising agent or a reducing agent, depending on the conditions and the nature of the dissolved substance. Under ordinary conditions, the oxidising power of HO_2[208] is close to that of Ce^{4+}. In oxidations HO_2 is converted into H_2O_2, and in reductions it is converted into H_3O^+ and O_2.

The reactions of HO_2 with the OH radical require special mention. Until recently it was assumed that this reaction takes place as follows:

$$HO_2 + OH \rightarrow H_2O + O_2. \qquad (35)$$

Kinetic proof has been obtained[379], however, of the formation of H_2O_3 by the combination of HO_2 and OH. The yield of H_2O_3 at pH 2–3 is 1.7. The pK value for the dissociation

$$H_2O_3 \rightleftarrows H^+ + HO_3^- \qquad (36)$$

is 9–10. The disappearance of H_2O_3 depends on the acidity of the medium. Its half-life is ~ 2 s in 0.02 M acid, and less than 0.1 s in 1 M and 10^{-4} M acid. This substance does not react with Ce^{4+}, tetranitromethane, or KI in neutral solution, but it oxidises Fe^{2+}. The formation and the stabilisation of compounds of the type H_2O_3 are observed[381] in various free-radical reactions on cooled surfaces.

TABLE 6. Rate constants for the reactions of perhydroxyl radicals in aqueous solution at 20–25°C.

Reaction	Medium	k, litres mole^{-1} s^{-1}	Ref.
HO_2+Fe^{3+}	0.5 M H_2SO_4	$7.3\cdot10^5$	382
HO_2+Cu^{2+}	pH 2.3	$1.5\cdot10^7$ *	383
$HO_2+MnO_4^-$	pH 3	$8\cdot10^6$	280
$HO_2+Br_2^-$	pH 2	$(1.6—6.4)\cdot10^9$	281, 318, 319
$HO_2+Br_3^-$	pH 2	10^8	319
HO_2+Br_3	pH 2	$1.5\cdot10^8$; $<4\cdot10^8$	281, 319
HO_2+CNS^-	pH 1	$1.6\cdot10^9$	316
$HO_2+C(NO_2)_4$	acidic	$<1.9\cdot10^4$	179
$O_2^-+C(NO_2)_4$	pH 5.6–6.2	$(1.9—2.0)\cdot10^9$	179, 92
HO_2+HO_2	pH$\leqslant$3	$(1.9—2.7)\cdot10^{6}$**	167, 379, 380, 383—385
$O_2^-+O_2^-$	pH$\geqslant$5	$(1.35—1.7)\cdot10^{7}$**	167, 377, 380, 384
$H_2O_2^++H_2O_2^+$	pH$<$1 0	$5\cdot10^5$	378

* Determined by the pulse radiolysis method.
** Includes the value of constants obtained without using ionising radiation.

TABLE 7. Properties of perhydroxyl radicals in water.

Property	Numerical value	Ref.
λ_{max} for HO_2 in H_2O (25°C)	230 nm	167
$\varepsilon^{HO_2}_{230}$	$1.15\cdot10^3$ litres mole^{-1} cm^{-1}	167
λ_{max} for O_2^- in H_2O (25°C)	240 nm	167
$\varepsilon^{O_2^-}_{240}$	$1,06\cdot10^3$ litres mole^{-1} cm^{-1}	167
$E^\circ(HO_2, H^+/H_2O_2)$ (oxidant)	—1.7 V	385
$E^\circ(H^+, O_2/HO_2)$ (reductant)	+0.3 V	385
pK ($HO_2 \rightleftarrows H^+ + O_2^-$)	4.4—4.5	167, 172, 379
pK ($H_2O_2^+ \rightleftarrows H^+ + HO_2$)	1.0	380

Table 6 gives absolute reaction rate constants for HO_2, O_2^-, and $H_2O_2^+$ radicals in aqueous solution, determined by various authors. The chief properties of perhydroxyl radicals in water are summarised in Table 7.

6. THE OXYGEN ATOM

The possible formation of atomic oxygen as a primary product of radiolysis has been postulated by a number of workers[238,385]. Allen[238] gives some indirect evidence for the production of O atoms in the decomposition of neutral water under the influence of radiation. He argues that, if it is assumed that H atoms are produced in yield 0.55 in neutral medium, $G(-H_2O)$ becomes 4.3. In this case, however, the oxidising products do not balance. To preserve the balance, it is necessary to assume the formation of another oxidising radiolysis product, which, from results for radiolytic transformations in a number of systems, should not react with hydrogen or ethanol, but is reactive towards hydrogen peroxide. Since in neutral medium $G_{OH} = 2.2$ and $G_{H_2O_2} = 0.7$, the yield of this product should be 0.7 equiv. eV^{-1}. If this product is atomic

oxygen, $G_O = 0.35$. Allen uses this hypothesis to explain various features of the radiolysis of a number of systems—H_2O_2–O_2 [57], NO [226], formate solutions [386], and H_2O_2 in H_2O. [18,387]

Allen [238] suggests the OH^+ ion as a possible source of atomic oxygen. Mass-spectroscopic data [388] in fact show that H_2O^+ and OH^+ ions (ratio 100 : 23.2 [289]) are formed in largest quantities in water vapour as a result of electron collisions (energy of electrons 100 eV). Baxendale and Gilbert [390] consider that OH^+ ions react in the gaseous phase with H_2O to give OH radicals:

$$OH^+ + H_2O \rightarrow H_2O^+ + OH \qquad (37)$$

but it has recently been shown experimentally [391] that this reaction produces H_3O^+ ions:

$$OH^+ + H_2O \rightarrow H_3O^+ + O. \qquad (38)$$

According to the data of Thynne and Harrison [391], in the gaseous phase $k_{38} = 2.9 \times 10^{11}$ litres mole^{-1} s^{-1}.

It is of course difficult to suppose that the relative proportions of H_2O^+ and OH^+ should be the same in the gaseous phase and in the liquid, but it may be assumed that the OH^+ ion is also produced by the action of radiation on liquid water. It may evidently then be a precursor of atomic oxygen. It is probable that in neutral medium OH^+ dissociates with the formation of O and H_3O^+ [reaction (38)]. In this connection it is interesting to note that the proposed ratio G_{OH}/G_O is close to the ratio of the quantities of H_2O^+ and OH^+ in the gaseous phase. It should be emphasised that the production of O by this mechanism should be accompanied by the formation of the same quantity of H:

$$H_2O \rightsquigarrow OH^+ + H + e^-. \qquad (39)$$

In acid medium, because of the presence of H_3O^+ ions, different routes for the disappearance of OH^+ are possible.

Another source of O atoms may be the recombination of OH radicals [392]:

$$OH + OH \rightarrow H_2O + O. \qquad (40)$$

Experiments [393,394] on the radiolysis of acidic and neutral water at high absorbed dose rates—i.e. under conditions where the recombination of radicals is highly probable—show, however, a significant increase in $G(H_2O_2)$ compared with low dose rates. It is thus unlikely that atomic oxygen is formed by the recombination of OH radicals.

There are at present no quantitative data on the properties of atomic oxygen in aqueous solutions. Taube [395], in a study of the reactions of excited O atoms (in the ^1D-state), showed that these atoms react readily with water to form hydrogen peroxide. In the ground state O atoms do not react with water. Katakis and Allen [396], studying the radiolysis of concentrated perchloric acid solutions, have observed not an increase but a decrease in $G_{H_2O_2}$ with increase in the $HClO_4$ concentration. In these solutions the direct action of radiation on perchloric acid produces excited perchlorate ions, which decompose to ClO_3^- and O. From the observed dependence of the yield of H_2O_2 on $[HClO_4]$, these workers conclude that the O atoms produced are in the ground state. Formation of O atoms is possible in the radiolysis of concentrated solutions of various other oxygen-containing anions (NO_3^-, $KMnO_4$, etc.).

7. EXCITED WATER

As already noted, the passage of ionising radiation through water leads to ionisation and excitation of H_2O molecules. The fate of the "excited water" and the part it plays have not yet been elucidated, however.

Excited water molecules may be formed [397] in two ways—(1) by capture of the ejected electron by the H_2O^+ ion (Samuel–Magee hypothesis), and (2) by collision of slow electrons with water molecules—and Magee [398] considers that water molecules in the singlet and triplet states may be produced in a spur, in the ratio 1 : 3, as a result of the first process.

Platzman [399] suggests that, in the gaseous phase, irradiation produces both ionised and excited molecules in equal yields. In the condensed phase "superexcited" molecules (their energy exceeding the ionisation potential) use up the excess of energy, not only for ionisation but also for other processes. For example, breakdown of the molecule into two radical fragments is possible. In Allen's opinion [1], however, excitation of H_2O to an upper electronic level in liquid water may lead to ionisation. According to Voevodskii [400,401] the excitation in liquid water may be transferred through hydrogen bonds and be localised at impurities, leading to the formation of H, OH, H_2, and H_2O_2. If the excitation of water does not lead to ionisation, the H and OH radicals formed by the breakdown of H_2O^* will be produced close to one another and will possibly, as a result of the "cage effect" [402], recombine for the most part, to re-form water. It is of course not excluded that a certain proportion of the H atoms, because of their very small dimensions, will escape from the "cages" into the bulk of the liquid, through the cavities in the quasi-crystalline water lattice. If, however, excitation of the water leads to ionisation (see footnote on p. 603), the H (or e^-) and the OH formed from the H_2O^* produced as a result of the capture of the ejected electron by H_2O^+ will be in the same small spur as the H_3O^+ and OH (from the H_2O^+), as is assumed by Matheson [403]. This also facilitates the H + OH reaction. These considerations lead to the conclusion that, in dilute solutions of ordinary substances, the part played by excited molecules is small. The radiolysis of concentrated solutions is quite different. As first postulated by Proskurnin [404–407], at high concentrations a solute can penetrate into the "cage", as a result of which its reaction with radicals becomes possible. Later, Bakh and his coworkers [408], Pikaev [409], Kabakchi [410,411], Sowden [412,413], and Katakis and Allen [396] attributed various features of the radiolysis of concentrated solutions to reactions in which H_2O^* takes part. Dainton and his coworkers [54,55] put forward similar explanations for the increase in the yields of radical products of the radiolysis of water in acid and alkaline media, and also in relatively concentrated N_2O solutions. Shubin and Dolin [414,415] observed a considerable increase in yields in a number of systems when these were saturated with inert gases under very high pressures. It was suggested that in these experiments ordering of the water structure takes place. This creates favourable possibilities for the transmission of excitation along a chain of hydrogen bonds. In the opinion of these authors, the excitation here appears in the form of exciton-like formations (electron–positive-hole pairs).

Recently, the idea that "excited water" takes part in radiation reactions has been introduced into the interpretation of certain features of the radiolysis of dilute aqueous

solutions of a number of substances. Hayon[78] considers that, in the radiolysis of neutral solutions, certain substances (e.g. O_2) may react directly with H_2O^*. Shinohara and his coworkers[416,417], in a study of the radiolysis of neutral or weakly acidic HgX_2–NaN_3 and HgX_2–$NaNO_2$ solutions, conclude that under the most favourable conditions about five excited water molecules per 100 eV absorbed energy may take part in radiolytic transformations. Anbar and Meyerstein[307,308,418], in an investigation of the influence of ions of the type Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} on the magnitude of G(HD) in irradiated solutions of 2-deuteriopropan-2-ol and methanol (0.01–0.1 M), have been forced to postulate the possibility of reactions between H_2O^* and these ions and alcohols. Shagisultanova et al.[419] attribute the hydrolytic decomposition of oxalato-complexes of Co^{III} in aqueous solution under the influence of ^{60}Co γ-radiation to the penetration of excited water molecules into the coordination sphere of these compounds. Getoff[420] assumes that the carboxylation of amines in aqueous solution is due partly to reactions involving H_2O^*. Kabakchi et al.[421,422] attribute the characteristic features of the radiolysis of the H_2O_2–O_2–H_2 system to the reactions of the dissolved substances with exciton-like formations.

There is at present no direct experimental proof of the formation of excited water molecules. Niira[423] has predicted theoretically that water has a triplet excited state, and Kuppermann[424], in a study of the scattering of electrons with energies of 25–100 eV in the gaseous phase, has detected an excited state of H_2O with an energy 4.2 ± 0.2 eV higher than the energy of the ground electronic state. Sitharamarao and Duncan[425], in an examination of the emission of light from water during γ-irradiation, conclude that H_2O^* and OH^* are formed in appreciable yield during the radiolysis of water. More recently, however, a similar investigation by Czapski and Katakis[426], carried out at a higher experimental level, has shown that the radiation yield of light emission is negligible ($\leq 10^{-5}$).

In the liquid phase an excited molecule in the triplet state has a lifetime of 10^{-4} s or more[427]. The possibility that this also applies to water cannot be excluded. It is evident that, as a result, these H_2O^* molecules may also take part in radiation reactions in comparatively dilute solutions. Chemically, however, H_2O^* molecules are generally equivalent to (H + OH), so that they should "develop" only with certain solutes[54,55]. This effect can be observed particularly clearly when the solution contains "conjugated acceptors"[404–407,428–431], i.e. when, as it were, both an acceptor for H atoms and an acceptor for OH radicals are present. At the same time it is necessary that a given acceptor be an effective excitation "quencher".

There are no experimental or theoretical data on the possibility of the existence of excitons in liquid water. According to Protopopov[432,433], free and local excitons may exist in aromatic liquids and solutions. In addition to the local exciton, the liquid also contains a state of local ordering, which is termed an orienton. The lifetime of these formations is short ($\leq 10^{-9}$ s), however. Davydov[434] considers that in some instances excitons of the Wannier–Mott type (an electron–positive-hole pair) may be produced in the liquid phase. Jortner[435] has recently carried out quantum-mechanical calculations and demonstrated the possibility of the existence of excitons in media of the liquefied inert gas type. For water, it is apparently necessary to make allowance for its high polarity. It follows from theory that the bond energy of the exciton decreases in proportion to the square of the dielectric constant of the medium[436]. Moreover, with marked polarisation, the bound electron and positive hole can in principle form a polaron pair[437]. Finally, it must be emphasised that water is characterised by a high reactivity towards H_2O^+ ions. It can therefore probably be concluded that, although water has a crystal structure with short-range order, excitons in it, if they are produced, have an extremely short lifetime, and in dilute aqueous solutions they break down (possibly to OH and e^-_{aq}) without being able to spread. These discussions are of course qualitative, and it would be extremely desirable for the appropriate quantum-mechanical calculations to be carried out.

In connection with the foregoing, considerable interest attaches to work[438–440] using the pulse radiolysis method, which has established the formation of triplet-excited molecules of naphthalene and other aromatic substances during irradiation of their solutions in benzene and cyclohexane. In aqueous solutions, however, the yields are negligible[439].

Thus excitation of water can be observed only under strictly specific conditions. In dilute aqueous solutions of ordinary substances, the part played by this process is small.

8. THE MOLECULAR PRODUCTS H_2 AND H_2O_2

Hydrogen and hydrogen peroxide are the primary molecular products of the radiolysis of water. Many workers[268,272,273,286–301,356,361,408,412,413,441–455] have shown that the yields of H_2 or H_2O_2 decrease with increase in the concentration of dissolved substances which are acceptors of H atoms (e^-_{aq}) or OH radicals respectively. The following relationship is observed

$$G_{R_2} = G^0_{R_2} - A[S]^{1/2}$$

where G_{R_2} is the yield of H_2 or H_2O_2 at a given concentration of the acceptor S, $G^0_{R_2}$ the yield of molecular product at zero concentration of the acceptor, [S] the molar concentration of the acceptor, and A a parameter defining the probability of interaction between the acceptor and the corresponding radical.

Byakov and his coworkers[456,457] have carried out a theoretical treatment of the dependence of G_{R_2} on [S] on the basis of a simplified diffusion–radical model for the radiolysis of water. They have shown that this dependence is given by the equation

$$G_{R_2} = G^0_{R_2} - G^0_{R_2}\left(\frac{k_{R+S}}{k_{R+R}}\frac{v_0}{n_0}\right)^{1/2}[S]^{1/2}$$

where n_0 is the initial number of radicals in the spur, v_0 is the initial volume of the spur, and k_{R+S} and k_{R+R} are the rate constants for the corresponding reactions. Byakov and Bugaenko[458] use this equation and the experimental dependence of G_{R_2} on [S] to calculate a large number of relative rate constants for radiation reactions. The calculated values are close to the experimental values. The agreement between the constants provides evidence in support of the hypothesis that at least the greater part of the H_2 and H_2O_2 is formed as a result of the recombination of radicals in the spurs [reactions (9–12)].

Weiss and Hayon[59], Hayon[459], and Rabani and Stein[212] postulated that a large proportion of the molecular hydrogen is formed as a result of the recombination of e^-_{aq} in

the spurs or at a short distance from the latter. Proof for the possibility of formation of H_2 from e^-_{aq} was obtained by Dorfman and Taub[30], who measured the yields of HD and D_2 in alkaline and acidic solutions of C_2H_5OD in D_2O. Production of H_2 occurs also[28,29] by the reaction of e^-_{aq} with H at sites of high radical concentration. The mechanisms of these two interesting reactions are still unknown, however. The recombination of e^-_{aq} possibly passes through a stage involving the formation of $(e^-_{aq})_2$. The production of such "bipolarons" was postulated in one of the theories of metal-ammonia solutions[460]. Anbar and Meyerstein[461,462] have studied the isotopic effect in the formation of hydrogen by the recombination of e^-_{aq}, and found that this effect is much greater than would be expected on the basis of the hypothesis that the H_2 is produced by the diffusion-controlled process $e^-_{aq} + e^-_{aq}$. They therefore conclude that the recombination of e^-_{aq} involves the formation of $(e^-_{aq})_2$, and that decomposition of the latter (into $H_2 + 2OH^-$) with rupture of the H–O bond takes place much more readily than the corresponding decomposition with rupture of the D–O bond. In the second reaction, the H^- ion is probably produced as an intermediate product.

There are other theories regarding the ways in which the molecular products of the radiolysis of water are produced. Many authors[245,388,459,461-465] suggest that H_2 and H_2O_2 may be produced by the decomposition of "excited water". Stein and his coworkers[387,463] have studied the radiolysis of H_2O_8 in $H_2{}^{18}O$. According to their data, one fraction of the H_2O_2 precursors is readily captured by acceptors of OH radicals, whereas the other fraction does not exhibit this property. These authors conclude that the yield of H_2O_2 corresponding to the second type of precursor (possibly H_2O^*) is about 0.4. Similar results[245] have been obtained in a study of the dependence of $G_{H_2O_2}$ on the concentration of $[Fe(CN)_6]^{3-}$. Here the yield of H_2O_2 corresponding to H_2O^* amounts to 0.3. It should be emphasised, however, that these values of the H_2O_2 yield, which are independent of the concentration of acceptors of OH radicals, are apparently too high. Czapski[466] has represented the results of published work[245,388,463] graphically by plotting $G_{H_2O_2}$ against $[S]^{1/3}$, and obtained an almost linear relationship. Some of these authors have subsequently[467] agreed with this conclusion. Anbar and Meyerstein[388,463,461,462] find that the isotopic effect in the formation of H_2 as a result of the radiolysis of water is much smaller than that for the recombination of e^-_{aq} obtained photochemically. On this basis they conclude that, in the irradiation of water, a large proportion of the H_2 is produced, not by the reaction $e^-_{aq} + e^-_{aq}$ in the spurs, but as a result of various other processes (e.g. the decomposition of "excited water"). It is undoubtedly extremely desirable to confirm this very interesting observation for a number of other materials, and to establish the fraction of H_2 and H_2O_2 produced from "excited water".

In Platzman's opinion[468], a certain proportion of the H_2 is formed by the reaction of underexcited electrons (of energy ≤ 6.5 eV) with water, with the intermediate formation of H^- ions. The calculations show that the yield of H_2 as a result of this reaction may reach 0.2 ± 0.1.

Molecular hydrogen generally does not react with dissolved substances. When the solution contains large quantities of H_2, however, or when no other acceptors of hydroxyl radicals are present, the hydrogen reacts with OH radicals, converting them into H atoms in acidic and neutral media, and into e^-_{aq} in alkaline medium.

Hydrogen peroxide may exhibit reducing properties or oxidising properties, depending on the nature of the dissolved substance and the pH of the medium†. Hydrogen peroxide undergoes electrolytic dissociation:

$$H_2O_2 \rightleftarrows HO^-_2 + H^+ \qquad (41)$$

the pK value for this reaction being 11.75.

9. MAXIMUM YIELD IN THE DECOMPOSITION OF WATER

The magnitude of $G(-H_2O)$ is determined by the ionisation of the water, without allowance for the reactions $H + OH$ and $e^-_{aq} + OH$ in the spurs. If we assume that in neutral water H is produced in addition to e^-_{aq}, we reach the conclusion that $G(-H_2O)$ depends little on pH. The values found for this yield are 4.55, 4.3, and 4.6–4.8 in acidic, neutral, and alkaline media respectively. It is difficult to make accurate allowance for the contribution of the reactions $H + OH$ and $e^-_{aq} + OH$, taking place in the spurs. According to Hochanadel[397], the yield for the decomposition of water $G'(-H_2O)$ with allowance for these reactions amounts to ~ 6. Diffusion-kinetic calculations carried out by Byakov et al.[457] show, however, that this yield may reach ~8. Various data provide evidence in support of this last value. Proskurnin and his coworkers[407,428,429] found that $G(NO_2^-)$ in concentrated (1 M and above) alkaline solutions of $NaNO_3$ saturated with nitrogen is 4.0–4.5 ions per 100 eV. If it is assumed that two reducing particles are used up in the formation of one nitrite ion, $G(-H_2O) \simeq 8$–9. Baxendale and Gilbert[390] studied the radiolysis of mixtures of the vapours of H_2O and methanol, ethanol, ether, or cyclohexane, and concluded that $G'(-H_2O) = 8.0 \pm 0.7$. According to Anderson et al.[470,471] in the gaseous phase in the presence of cyclohexane or ammonia $G(-H_2O)$ has the values 7.0 (over the range 125–250°C) and 10.6 (above 300°C).

Firestone[472] studied the formation of HD in mixtures of gaseous D_2 and water vapour containing tritium, and found that $G(HD) = 11.7 \pm 0.6$. If it is assumed that the HD is produced as a result of the reaction $H + D_2$, it is obvious that $G(HD) = G(-H_2O)$. Baxendale and Gilbert[390], discussing these results, have suggested that, in the D_2–H_2O system, isotopic exchange by deuterium involves both ionised and excited water molecules. If this is so, the difference between the yields for the decomposition of water, observed in these experiments, gives the yield of excited molecules. This difference is ~4. The same value for the H_2O^* yield can be obtained by examining the results of work by Proskurnin and his coworkers[407,428,429]. These authors found that $G(NO_2^-)$ in concentrated alkaline solutions of $NaNO_3$ increases to ~6 ions per 100 eV when a "conjugated acceptor"—glycerol or glucose—is added. Finally, it has been shown[414,415] that under certain conditions the yield for the decomposition of water may reach ~14.

Thus definite data have now been obtained, indicating that the maximum yield for the decomposition of water amounts to 12–14 molecules per 100 eV. The maximum yield due to ionisation is 6–8 molecules per 100 eV. It is evident that in dilute solutions these yields can be achieved only in exceptional instances, if at all.

† The properties of hydrogen peroxide have been described in detail in a monograph[469].

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VIBRATIONAL AND ELECTRONIC SPECTRA OF AROMATIC SIX-MEMBERED AZACYCLIC COMPOUNDS

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INTRODUCTION

Six-membered aromatic azacyclic compounds occur as structural units in a large number of more complicated compounds having important and diverse applications. These molecules are present in biologically active substances[1,2]. For example, thymine and cytosine, component parts of deoxyribonucleic acids (DNA)[3-5], are pyrimidine derivatives. Pyrazine derivatives are widely used in the synthesis of medicinal preparations and dyes[6]. Although pyridine and the diazines have been known for a long time, free symmetrical triazine was discovered only in 1953, by Grundmann and Kreutzberger[7]; its physical and chemical properties were soon studied in detail, and have been described in a review by Finkel'shtein and Boitsov[8]. Apart from their varied practical applications, these substances are of great interest also for the further development of the theory of chemical structure.

One of the chief physical methods for studying molecular structure is the application of spectroscopy, and during recent years a large amount of theoretical and experimental research has been done on the vibrational and electronic spectra of six-membered aromatic nitrogen heterocycles. The present review is devoted to their interpretation and systematisation. It consists of two parts: the first discusses the vibrational spectra of pyridine, and three diazines, triazine, and tetrazine; and the second part gives an analysis of the absorption and luminescence spectra of the same compounds. The review covers all the important experimental papers and calculations completed up to 1966.

I. VIBRATIONAL SPECTRA

1. Geometrical Structure of Azines and Classification of Vibrations

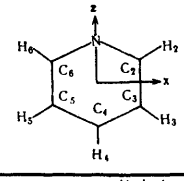
The replacement of one or more carbon atoms in the benzene ring by nitrogen atoms results in a change in the force field and distortion of the ring from the regular hexagon form. All azine molecules are planar. The bond lengths and valency angles have been determined by various physical methods—X-ray examination, electron diffraction, microwave spectroscopy, study of the rotational structure of the electronic spectra—and a complete list of all the geometrical parameters of the azines has been compiled by Berezin[9] (Tables 1 and 2). Experimental data on the geometrical structure of pyridazine are lacking.

The coordinate axes indicated in Tables 1 and 2 have been used in the classification of the normal vibrations of azines according to symmetry types. The symmetry group and the types of vibration are given below for each of the molecules.

Pyridine C_{2v}, $10A_1 + 3A_2 + 9B_1 + 5B_2$.
Pyrimidine C_{2v}, $9A_1 + 2A_2 + 8B_1 + 5B_2$.
Pyridazine C_{2v}, $9A_1 + 4A_2 + 8B_1 + 3B_2$.
Pyrazine D_{2h}, $5A_g + 2A_u + 4B_{1g} + 2B_{1u} + B_{2g} + 4B_{2u} + 2B_{3g} + 4B_{3u}$.
1,3,5-Triazine D_{3h}, $3A_1' + 2A_2' + 2A_2'' + 5E' + 2E''$.
1,2,4,5-Tetrazine D_{2h}, $4A_g + A_u + 3B_{1g} + 2B_{1u} + 3B_{2u} + 2B_{2g} + 3B_{3u}$.

Vibrations of the symmetry types A_1, B_1, A_g, B_{1g}, B_{2u}, B_{3u}, A_1', A_2', and E' are planar, whereas the remaining vibrations are non-planar. The vibrations E' and E'' are doubly degenerate. All vibrations of molecules with symmetry C_{2v}, vibrations having the subscript g, and the vibrations A_1, E', and E'' are active in the Raman spectra. The vibrations A_1, B_1, and B_2, vibrations having the subscript u, and the vibrations A_2'' and E' are active in the infrared spectra. Vibrations of types A_u and A_2' are forbidden by the selection rules, and are inactive in vibrational spectra of both types.

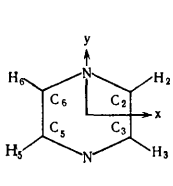
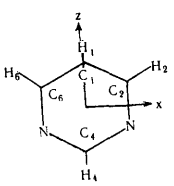
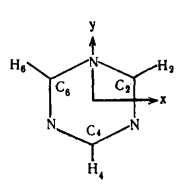
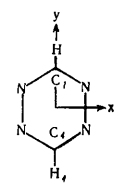
TABLE 1. Bond lengths (Å) and valency angles in the pyridine molecule according to various authors*.



Bonds and angles	Method					
	electron diffraction (Ref. 10)	microwave spectrum (Ref. 12)	microwave spectrum (Ref. 14)	microwave spectrum (Ref. 12)	electron diffraction (Ref. 14)	calc. (Ref. 15)
C_2-H_2	1.090	1.080	1.080	1.085	1.078	1.092
C_3-H_3	1.090	1.080	1.080	1.080	1.078	1.080
C_4-H_4	1.090	1.080	1.080	1.075	1.078	1.080
$N-C_2$	1.370	1.350	1.355	1.342	1.377	1.355
C_2-C_3	1.405	1.390	1.390	1.391	1.377	1.397
C_3-C_4	1.405	1.390	1.390	1.398	1.377	1.397
C_6NC_2	119°	117°	115°30′	116°42′	—	114°46′
NC_2C_3	121°	123°	—	124°	—	125°04′
$C_2C_3C_4$	121°	119°48′	—	118°36′	—	118°23′
$C_3C_4C_5$	121°	117°24′	—	118°06′	—	118°20′
NC_2H_2	—	—	—	115°44′	—	114°18′
$C_3C_2H_2$	—	—	—	120°16′	—	120°38′
$C_2C_3H_3$	—	—	—	120°17′	—	120°30′
$C_4C_3H_3$	—	—	—	121°07′	—	121°07′
$C_3C_4H_4$	—	—	—	120°57′	—	120°50′

* References 11 and 13 appear to be omitted from the text; the former refers to an electron diffraction study of pyridine; the latter refers to the study of the microwave spectrum of pyridine (Ed. of Translation).

TABLE 2. Bond lengths (Å) and valency angles in pyrazine, pyrimidine, 1,3,5-triazine, and 1,2,4,5-tetrazine.

Bonds and angles	Pyrazine			Pyrimidine*	1,3,5-Triazine		1,2,4,5-Tetrazine*
							
	electron diffraction (Ref. 10)	X-ray diffraction (Refs. 17,18)	rotational structure of ultraviolet spectrum (Ref. 19)	X-ray diffraction (Ref. 16)	X-ray diffraction (Ref. 20)	Raman rotational spectrum (Ref. 21)	electron diffraction (Ref. 22)
$C_1—C_2$				1.38			
$C_2—C_3$	1.39	1.378	1.395	1.41			
$C_2—N$				1.35			
				1.36			
C—N	1.35	1.334	1.341	1.33	1 319	1.338	1.334
				1.34			
N—N							1.321
C—H	1.09	1.05	1.085		1.00	1.084	
CNC	120°	115°66′	116°	115°12′	113°12′	113°12′	
				115°06′			
NCN				128°12′	126°48′	126°48′	127°22′
CCN	120°	122°24′	122°	122°30′			
				122°42′			
CNN							115°57′
CCC				116°18′			
NCH		116°54′					
CCH		120°18′					

* The numbering of the atoms in the formula does not correspond to the standard numbering for nomenclature purposes (Ed. of Translation).

2. Experimental Data on Vibrational Spectra and Their Interpretation

(*a*) Pyridine. Many investigations have been made of the Raman spectrum of pyridine [23-30], in all of which the intensity was merely estimated qualitatively or on a denary scale. Depolarisation measurements were made [23,24] only for a very few lines, and the results did not give the true depolarisations. Only one paper [31] has given quantitative data for standard intensities and true depolarisation measurements, together with the Raman line widths.

Determinations have been made of the infrared spectra of pyridine vapour [32,27] and liquid pyridine [24,27,33-35]. Interpretation of the vibrational spectra became considerably more reliable after examination of the Raman and infrared spectra of pentadeuteriopyridine [24], and of 4-mono- and 2,6- and 3,5-di-deuteriopyridines in liquid and vapour states [29]. The infrared spectrum of pyridine vapour itself was also obtained in the latter work [29]. The infrared spectra of the above two dideuteriopyridines in both states have subsequently been examined in detail [36]. In another case the infrared spectra of the three monodeuteriopyridines were obtained [37].

Before the problem of the normal vibrations of pyridine and its deuterio-derivatives was solved, the interpretation of the vibrational spectra had been based on the product rule for the frequencies of isotopic molecules, selection rules, comparing the spectra of pyridine and deuteriopyridines with thoes of benzene and deuteriobenzenes, and comparing the infrared and Raman spectra of pyridines in liquid and vapour states [24,29]. A theoretical calculation [36] of the vibration frequencies of pyridine and pentadeuteriopyridine using the force constants of benzene did not give satisfactory results. A complete calculation of all the vibration frequencies of pyridine and the deuteriopyridines has been reported for the first time [38]. A solution has been obtained [39] to the problem of the non-planar vibrations of pyridine and the deuteriopyridines, with a determination of the system of force constants, and also for the planar vibrations [40]. A fresh calculation has been made [41] of the planar vibration frequencies of pyridine and pentadeuteriopyridine using the force constants of benzene. The frequencies and modes of vibration of 4-deuteriopyridine and of 2,6- and 3,5-dideuteriopyridines, together with the atomic displacements in all 27 vibrations of pyridine itself, these three deuterio-derivatives, and pentadeuteriopyridine, have been calculated [42] using the force constants of benzene. The Urey–Bradley potential function has been applied [43] to the calculation of the frequencies of the same molecules. An advantage of such a function is the smaller number of force constants involved, compared with the complete quadratic potential function in the valency–force system of vibrational coordinates. However, as discussions during recent years have shown, this advantage is ineffective, since the Urey–Bradley force constants have no real physical meaning. It is not suprising, therefore, that sufficiently good agreement was not achieved [43] between calculated and experimental frequency values.

The most complete interpretation of the vibrational spectra of pyridine and the deuteriopyridines has been given by Berezin [39,40,9]. Its reliability is based on a complete solution of the converse vibrational problem—calculation of the vibrational modes and the atomic displacements during vibration—and is confirmed by good adherence to the product rules and Sverdlov's addition rules for the squares of frequencies [44] and the frequencies themselves [45] for isotopic molecules and Brodersen and Langseth's complete isotopic rule [46].

(*b*) Pyrimidine. The experimental data are far more limited than in the case of pyridine. The Raman spectra of liquid pyrimidine have been obtained[47,48], and an interpretation has been suggested[48] for the spectra. The absorption curve has been given[49] over the range 750–2000 cm^{-1}. Separate narrow portions of the infrared spectrum have been studied[50–53], and a more detailed investigation of the infrared spectrum has been made[47]. Several vibration frequencies have been obtained from the phosphorescence spectrum recorded at a low temperature[54]. The frequencies and vibrational modes have been calculated, and the vibrational spectra interpreted[55]. The frequencies and band intensities of the non-planar vibrations of pyridine, pyrimidine, and their methyl derivatives have been compared[56] with the corresponding frequencies and intensities for benzene and its substituted derivatives. This comparison introduced certain changes into the previously accepted interpretation of individual bands, but we are unable to go into these details.

(*c*) Pyridazine. The Raman and infrared spectra of liquid pyridazine have been obtained[47,48]. In the first of these papers[47] only five frequencies were found in the Raman spectrum, while the infrared spectrum was examined only in the range $\nu > 650$ cm^{-1}. The second paper[48] reported a more detailed study of both spectra, the infrared spectrum beginning at 370 cm^{-1}, and an assignment of frequencies to symmetry types was suggested. The whole system of fundamental frequencies has been calculated[57].

(*d*) Pyrazine. The Raman and infrared spectra have been obtained[47]. Another paper[48] reports both infrared and Raman spectra of liquid pyrazine, together with the infrared spectrum of its vapour. Several vibration frequencies have been determined from the low-temperature phosphorescence spectrum[58,59]. None of these investigations gives a complete system of fundamental frequencies, but they mutually complete the vibrational spectrum.

The first theoretical interpretation was based[48] on selection rules (rule of mutual exclusion), intensities and depolarisations, and comparison with the spectra of benzene and pyridine. This approach does not solve the problem, but it serves as an important prerequisite for a theoretical calculation. The first such calculation[60] used the force constants of benzene, and did not give satisfactory agreement between calculated and experimental frequencies. New calculations have been made[61,62] of the frequencies of non-planar and planar vibrations. The most complete solution of the problem of non-planar and planar vibrations with the full quadratic potential function has been accomplished[63,64] by calculation of the derivatives of the frequencies with respect to the force constants. Nevertheless, the interpretation given in these papers cannot be regarded as definitive, since the number of force constants to be determined exceeded the number of frequencies. In this case neither the force constants themselves nor the frequency assignments were determined unambiguously.

New opportunities for theoretical calculations were opened up by the determination of the vibrational spectra of the deuteriopyrazines. The Raman spectra[65] of pyrazine and tetradeuteriopyrazine in the liquid state and the infrared spectra of the latter compound in both liquid and vapour states permitted a detailed discussion of the various ways in which individual frequencies could be assigned taking into account the product rule and the assignment of combination frequencies. In an investigation[66] of the infrared spectra of pyrazine, *cis*-di-, and tetra-deuteriopyrazines in vapour and solid states, over the wide range 400–4000 cm^{-1}, frequency assignment was partly based on such new data as measurements of the dichroism of oriented crystals, analyses of rotational band envelopes, and polarisation measurements. These characteristics enabled pyrazine frequencies of symmetry types B_{1g}, B_{2g}, and B_{3g}, which were inactive in the infrared spectrum, to be determined. Finally, some additional information on the vibrational frequencies of pyrazine could be obtained from an analysis of the vibrational structure of its ultraviolet absorption spectrum[67,68] and a comparison of the frequencies of the ground and excited electronic states. In spite of such diverse approaches to the problem, a final solution was not achieved, since the interpretations of different authors did not agree among themselves.

A fresh theoretical calculation of the planar vibration frequencies of pyrazine, *cis*-di-, and tetra-deuteriopyrazine has been made[69] both with a valence-force potential function and with the Urey–Bradley potential function. The fact that both methods yielded the same frequency assignments is reassuring. Nevertheless, in many cases this assignment contradicts the results of other authors. It is obviously an urgent task to obtain the Raman spectrum of dideuteriopyrazine and to make fresh theoretical calculations in which all the isotopic rules are taken into account.

(*e*) 1,3,5-Triazine. The first determination of the Raman and infrared spectra was accompanied[70] by the first suggested assignment of the frequencies. Other analyses of these spectra were made[71,72], but in the most complete investigation of both spectra for both the triazine and the corresponding trideuteriotriazine[73] the infrared spectra were obtained for both liquid and gaseous states, and an approximate calculation was also made of the vibration frequencies. The planar vibration frequencies for both compounds have been calculated[74] by means of the Urey–Bradley potential function, but the resulting frequency assignments showed poor agreement with the addition rule for the frequencies of isotopic molecules. An attempt has been made[75] to solve the converse vibrational problem by determining 19 force constant, but such a solution cannot be regarded as complete. Solutions of the problems concerning the non-planar and planar vibrations have been obtained for both molecules[63,64] with the force constants of pyridine as zero-approximation constants.

(*f*) 1,2,4,5-Tetrazine. Infrared spectra have been investigated[76] for the symmetrical tetrazine and its mono- and di-deuterio-derivatives. Those of tetrazine itself in the range 700–3070 cm^{-1} were recorded for three states—the frozen solid phase, a solution in carbon tetrachloride, and the vapour—but those of the deuterio-derivatives were obtained not for the isotopically pure substances but for mixtures containing various percentages of tetrazine and mono- and di-deuterio-tetrazines, which made interpretation extremely difficult. As far as we are aware, the Raman spectrum of 1,2,4,5-tetrazine has not been obtained, but several frequencies, which should be active in the Raman spectrum, appear as weak lines in the infrared spectrum, thus infringing the rule of mutual exclusion. Some additional results for the assignment of frequencies have been obtained from analysis of the vibrational structure of the ultraviolet absorption bands[77,78] of symmetrical tetrazine and dideuteriotetrazine. The above limited spectroscopic data, together with the product rule and a solution of the problem of the normal vibrations of 1,2,4,5-tetrazine[64], has enabled an interpretation of its

TABLE 3. Interpretation of vibrational spectra of azines.

Benzene			Pyridine			Pyrimidine			Pyridazine			Pyrazine			1,3,5-Triazine			1,2,4,5-Tetrazine	
sym.* type	Wilson No.	ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	Raman ν, cm^{-1}	infrared ν, cm^{-1}	sym. type	infrared ν, cm^{-1}
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
E_u^{-I}	20b	3080	B_1	3090 (2)	3080 (v.s.)	B_1		3095 (m.)	A_1	3063 (5p)	3062 s.	B_{3u}		3070 (v.s.)	E'		3056 (s.)		
E_u^{-II}	20a	3080	A_1	3069 (0)		A_1	3083 (1)								E'		3056 (s.)	B_{3u}	3070 (m.)
A_{1g}	2	3062	A_1	3054 (8; 0.36)	3055 (s.)	A_1	3048 (10p)	3047 (s.)	A_1	3043 (6p)		A_g	3060 (9p)		A_1'	3042 (10p)			
B_{1u}	13	3060	A_1	3054 (8; 0.36)	3055 (s.)	A_1	3001 (1)		B_1		3075 (v.s.)	B_{3u}	(3090)					A_g	3040 (w.)
E_g^{+II}	7b	3047	B_1	3035 (0)	3036 (v.s.)	B_1				3043		B_{1g}	3060 (9p)						
E_g^{+I}	8a	1596	A_1	1580 (5; дп?)	1583 (v.s.)	A_1	1566 (5)	1570 (v.s.)	A_1	1578 (2)	1572	A_g	1584 (3p.)		E'	1555 (3dp)	1556 (s.)	A_g	(1489)
E_g^{+II}	8b	1596	B_1	1572 (5)	1572 (m.)	B_1	1566 (5)	1570 (v.s.)	B_1	1565 (3)	1565 (s.)	B_{1g}	1523 (3dp)		E'	1555 (3dp)	1556 (s.)	B_{1g}	(1543)
E_u^{-II}	19a	1485	A_1	1480 (2; 0.26)	1482 (s.)	A_1	1466 (1)	1467 (s.)	A_1	1446 (1)	1444 (s.)				E'	1410 (2dp)	1410 (v.s.)		
E_u^{-I}	19b	1485	B_1	1437 (0)	1441 (v.s.)	B_1	1398 (0)	1402 (v.s.)	B_1		1414 (s.)	B_{2u}		1413 (v.s.)	E'	1410 (2dp)	1410 (v.s.)	E_{2u}	1434 (w.)
A_{2g}	3	1326	B_1	1288 (1)	1296 (v.s.)	B_1	(1304)	(1304)	A_1	1283 (3)	1283 (s.)	B_{1g}	(1350)		A_2'	1278 (00)		B_{1g}	1278 (w.)
B_{2u}	14	1310	B_1	1224	1226	B_1	1227 (3)	1227 (s.)	B_1	1239 (2)		B_{3u}		1346 (v.w.)					
E_g^{+I}	9a	1178	A_1	1218 (5; 0.74)	1217 (s.)	A_1	1137 (4p)	1141 (s.)	A_1	1158 (6p)	1160 (m.)	A_g	1232 (2p)		E'	1176 (2dp)	1174 (m.)		
E_g^{+II}	9b	1178	B_1	1145 (1; dp)	1148 (s.)	B_1	1145 1160 (1)	1161 (s.)				B_{3u}		1490 (s.)	E'	1176 (2dp)	1174 (m.)	B_{3u}	1187 (v.s.)
E_u^{-I}	10b	1037	B_1		1081	B_1		1071 (s.)	A_1	1063 (8p)	1063 (s.)				A_2'		1068 (w.)	B_{2u}	1085 (m.)
E_u^{-II}	18a	1037	A_1	1068 (1)	1068 (s.)		1074 (8)		B_1		1052 (m.)	B_{2u}		1135 (s.)				B_{2u}	1106 (v.s.)
B_{1u}	12	1010	A_1	1030 (10, 0.05)	1030 (v.s.)	A_1	1053 (8p)	1055 (m.)	B_1	1006 (2)	1009 (v.s.)	B_{1u}		1021 (v.s.)	A_1'	1132 (8p)	1132 (v.w.)	B_{2u}	1200 (v.s.)
A_{1g}	1	992	A_1	991 (10; 0.05)	991 (v.s.)	A_1	991 (10p)	991 (s.)	A_1	962 (7p)	964 (s.)	A_g	1015 (9p)		A_1'	992 (7p)		A_g	990 (v.w.)
E_u^{+II}	17a	970	A_2	979 (1)	981 (w.)	A_2	870 (0)		B_2		987 (w.)	A_u	(950)		E''		830 (m.)		
B_{2g}	5	985	B_2	933 (1)	938 (v.w.)	B_2		980 (w.)	A_2	936 (1)		B_{3g}	753 (1)		A_2''		925 (v.w.)	B_{3g}	925 (m.)
E_g^{-I}	10a	849	A_2	883 (2)	883 (v.w.)				A_2	906 (1)		B_{2g}	925 (1dp)			(m.)			
E_g^{-II}	10b	849	B_2	883 (2)	883 (v.w.)	B_2	814 (0)	806 (s.)										B_{1u}	800 (v.s.)
B_{3g}	4	703	B_2	748 (0)	749	B_2	724 (1)	722 (v.s.)	A_2	751 (1)		B_{3g}	703 (3dp)		A_2''		737 (s.)		
A_{2u}	11	671	B_2	705 (0)	703 (v.s.)	B_2	679 (6)	679 (m.)	B_2		760 (v.s.)	B_{1u}		786 (v.s.)				B_{3g}	(775)
E_g^{+II}	6b	606	B_1	652 (5; 0.84)	653 (w.)	B_1		667 (s.)	A_1	661 (2dp)	664 (m.)	B_{1g}	641 (1)		E'	676 (6dp)	657 (s.)	B_{1g}	(679)
E_g^{+I}	6a	606	A_1	602 (2; 0.75)	604 (s.)	A_1	623 (2 dp)	624 (v.s.)	B_1	619 (2dp)	619 (v.s.)	A_g	609 (1)		E'	676 (6dp)	657 (s.)	A_g	737?
E_u^{+I}	16b	405	B_2	404 (1dp)	405 (s.)	B_2		344 (v.s.)	A_2	421 (1)		B_{1u}		417 (v.s.)	E''	340 (4dp)		B_{1u}	(340)
E_u^{+II}	16b	405	A_2	377		A_2	394 (2)		B_2	367 (2dp)	370 (s.)	A_u	(400)		E''	340 (4dp)		A_u	(319)
												B_{2u}		1063 (v.s.)	E'		830 (m.)		

* sym. = symmetry; v.s. = very strong; s. = strong; m. = medium; w. = weak; v.w. = very weak; p. = polarised; dp. = depolarised.

vibrational spectrum to be obtained which must be regarded as tentative. To refine this, the Raman spectrum must be obtained, and fresh calculations made.

We have been able to deal only briefly with the evolution of our knowledge of the vibrational spectra of the azines, without discussing individual frequencies. The results of comparing all the spectra and calculations of the frequencies and modes of the vibrations together with the atomic displacements during vibrations are listed in Table 3, which contains 27 fundamental frequencies for pyridine, 24 for each of the diazines, and 21 and 18 for symmetrical triazine and tetrazine. In Table 3 the frequencies of all the azines are compared among themselves and with those of benzene, for which the generally accepted Wilson numbers[79] are indicated. The symmetry types are given for each molecule. Table 3 permits the variation in frequencies to be traced in a series of azines. Unfortunately, owing to lack of space, we have not included the frequencies of the deuterioaxines in Table 3.

3. General Characteristics of the Force Field in Azine Molecules

It has now been established that vibrational spectra provide a great deal of information about the force fields in molecules. Indeed, the complete solution of the vibrational problem, with the establishment of a set of force constants and weighting coefficients [sic], permits conclusions to be drawn concerning the distribution of forces in a molecule and the variations in the force field occurring in series of compounds. Thus it follows from a comparison of these characteristics for benzene and pyridine that replacement of a carbon by a nitrogen atom leads to a breakdown in the equivalence of the bonds forming the ring. The carbon–nitrogen bond is more elastic than the remaining cyclic bonds or the carbon–carbon bond in benzene. The angles also become more elastic. The carbon–nitrogen bond exerts a greater resistance to displacement out of the plane of the ring than does the carbon–carbon bond. At the same time the interactions of non-adjacent structural units

of the ring are weakened in comparison with the corresponding interactions in benzene, which can be explained qualitatively by the greater degree of localisation of the π-electrons in pyridine. The CNC angle is, like the carbon–nitrogen bond, exceptional in its properties, which is obviously connected with the role of the lone pair of electrons on the nitrogen atom. The result is that the interaction of adjacent bonds in the ring is weaker if their common atom is nitrogen. The interaction of non-adjacent internal angles among themselves and with the external angles becomes weaker as the number of nitrogen atoms in the ring increases. These conclusions have been reached predominantly on the basis of an analysis of systems of weighting coefficients[9]. Comparison of them with other characteristics of the molecules (bond lengths and energies, atomic charges, bond orders) indicates a correlation with these parameters. It is especially interesting that a correlation has been established between the properties of the weighting coefficient of each nitrogen ring and its aromaticity, as well as with the Hammett σ-constants[9].

4. General Features of Vibrational Spectra of Azines

A comparative analysis of the vibrational spectra of benzene and the azines, together with calculations of the vibrational modes and the atomic displacements, enable the following generalisations to be made

(*a*) On passing from benzene to the nitrogen rings, the degeneracy is eliminated from ten degenerate vibrations of benzene. Each doubly degenerate frequency is split into two components (with the exception of 1,3,5-triazine). The magnitude of the splitting is small, but depends on the number and positions of the nitrogen atoms.

(*b*) Many vibrations of the nitrogen rings and the benzene ring are similar in mode and atomic displacements. The actual frequencies are also close to one another, and can be subdivided into the following groups (cm^{-1}).

1600–1500.	Planar stretching–deformation vibrations with varying participation of the bonds forming the ring, and of its external and internal angles. These lines are intense in both Raman and infrared spectra.
1500–1400.	Planar deformation–stretching vibrations with CCH angles predominantly involved. They are characterised by high intensity in the infrared spectrum.
1200–1060.	Planar stretching–deformation vibrations of the carbon–nitrogen skeleton.
1010–960.	Planar stretching vibrations of the ring bonds. They are distinguished by high intensity in the Raman and infrared spectra.
740–600.	Planar vibrations of the internal angles of the ring. The intensities vary in the series of nitrogen rings.
760–670. 420–320.	Non-planar vibrations of the carbon–carbon, carbon–nitrogen, and nitrogen–nitrogen bonds. They relate partly also to non-planar vibrations of carbon–hydrogen bonds. Frequencies in the first of these ranges are usually distinguished by high intensity in the infrared spectra

Besides the classification of frequencies according to vibrations of bonds and angles individual azines can be identified[80–88] from sets of frequencies However, discussion of this analytical problem lies outside the scope of the present paper.

II. ELECTRONIC SPECTRA

A. EXPERIMENTAL WORK ON ABSORPTION AND EMISSION SPECTRA

1. Pyridine

(*a*) Spectra of vapour. The early investigators[89–92] of the spectra of the vapour encountered difficulties in the range 3000–2400 Å in arranging the large number of lines observed in electronic–vibrational progressions having a common origin. Vibrational analysis of the bands showed[93] that two electronic transitions are apparent in this range, with frequencies of the 0–0 bands at 34 769 and about 38 350 cm^{-1}. Two band systems correspond to them—a very weak system, masked by a stronger diffuse system in the short-wavelength part of the spectrum—the first of which has no analogue in the spectrum of benzene, whereas the second system is analogous to the absorption of benzene in the region of 2600 Å. The similarity between the spectrum of pyridine in the region of 2500 Å and the absorption of benzene at 2600 Å was noted by another worker[94]. Extension of the spectral range to 1500 Å revealed[95] two new ranges of absorption, at 47 800–54 500 and 54 500–64 000 cm^{-1}. Estimates were made in this paper also of the oscillator strengths. Subsequent analysis[96] over the range 1800–1600 Å showed the presence of at least three band systems—sharp, diffuse, and continuous—so that the absorption spectrum contains five band systems—two sharp systems at 34 769 and 54 000 and three diffuse systems at 39 000, 49 769, and 56 405 cm^{-1}—and comparison of this spectrum with those of other aromatic compounds[97] indicates the possibility of using it for analytical purposes.

(*b*) Spectra of solutions. To determine the nature of the absorption spectrum and of the individual bands, it was important to investigate solvent effects on the spectrum. The spectrum of a solution in heptane was first studied[98], and subsequently that of an aqueous solution[99]. The spectra in many solvents showed[92,95,100,101] that the absorption maxima shift little, while the intensities increase in the sequence—hydrocarbons, water, alcohols, acids—a generalisation which has been used[102] to determine the acid–base properties of various substances with respect to pyridine. The absorption at 34 769 cm^{-1} disappears in polar solvents[100].

2. Diazines

(a) Spectra of vapours. The early investigations of the near ultraviolet absorption of pyrimidine[103], pyridazine, and pyrazine[104] showed the presence of two band systems—diffuse and sharp—in each case. The former corresponds to the absorption of benzene at 2600 Å, while the latter occurs at longer wavelengths. Analyses have been made of the vibrational structure of the sharp (3200 Å)[19,105–107] and diffuse[108] band systems of pyrazine.

TABLE 4. Interpretation of the electronic spectra of the azines.

Compound	Band characteristics	B_a and B_b bands (Refs. 68, 72)		Rydberg series, vapour Ref. 68	L_a bands (Refs. 68, 172)			L_b bands for solutions in (Refs. 68,101,127,138,172)					Solutions and vapour (Refs. 107, 127, 134, 138, 174)				
								solvents:									
		vapour	calc.		vapour	calc.	vapour	C_nH_m	water	alcohol	acid	calc.	aqueous	alcoholic	vapour	C_nH_m	calc.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
						$\pi-\pi^*$ Transitions									$n-\pi^*$ Transitions		
Pyridine	symmetry and polarisation		$^1B_1, x$ $^1A_1, z$		$^1A_1, z$				$^1B_1, x$						$^1B_2, y$		
	position of 0–0 band, Å	1773	1726 1704	1852	2009	1975	2564					2470			2876	2904	2910
	position of maximum, Å	1716														2703	
	ε_{max}							2520 2090	2530 3000	2530 3600							
	oscillator strength	1.3	1.092 1.132	1.3	0.20	0.045		0.03				0.043				0.03	
Pyrimidine	symmetry and polarisation		$^1A_1, z$ $^1B_1, x$		$^1A_1, z$				$^1B_1, x$								
	position of 0–0 band, Å	1705	1732 1667	1777	1911	1920	2481					2435			$^1B_2, y$ 3218	3246	3064
	position of maximum, Å	1666						2430	2430	2430	2420		2710	2800	2960	2985	
	ε_{max}							2030	3210	2920	5540		422	373		326	
	oscillator strength	1.0	1.061 1.125	(0.25)	0.16	0.001	0.044					0.052				0.0069	0.0072
Pyridazine	symmetry and polarisation		$^1B_1, x$ $^1A_1, z$		$^1B_1, x$				$^1A_1, z$						$^1B_2, y$		
	position of 0–0 band, Å	1745	1745 1697		(2000)	1980	2532					2460			3752	(3732)	3831
	position of maximum, Å	1695						2460	2470	2460	2380		3000	3110	3251	3400	
	ε_{max}							1300	1090	1160	1610		320	303		315	
	oscillator strength	(1.0)	1.092 1.117		1.10	0.34	0.020					0.024				0.0058	0.0083
Pyrazine	symmetry and polarisation		$^1B_{3u}, x$ $^1B_{2u}, y$			$^1B_{2u}, y$			$^1B_{3u}, x$						$^1B_{1u}, z$		
	position of 0–0 band, Å	1646 1620	1644 1614	1813	1966	1955	2580 2580	2600	2610	2610	2500 2820		3049	3100	3239	3278	3150
	ε_{max}							5600	5800	6000			850	860			
	oscillator strength	1.0	0.987 0.972	(0.25)	0.145	0.134	0.1					0.139				0.010	0.011
1,3,5-Triazine	symmetry and polarisation		$^1E', x, y$		$^1A_1'$				$^1A_2'$						$^1A_2'', z$		
	position of 0–0 band, Å		1625			1808						2265			3167	3192	3141
	position of maximum, Å							2220	2210	2210			2600	2670		2719	
	ε_{max}							146	183	213			747	768		881	
	oscillator strength		1.07			0						0				0.018	0.014
1,2,4,5-Tetrazine	symmetry and polarisation		$^1B_{2u}, y$ $^1B_{3u}, x$			$^1B_{2u}, y$			$^1B_{3u}, x$						$^1B_{1u}, z$		
	position of 0–0 band, Å		1739 1585			1907						2551			5514	5593	4770
	position of maximum, Å							2520	2530				5102		5514	5387	
	ε_{max}							2150	2840				362			829	
	oscillator strength		1.012 1.179									0.123				0.0042	0.011

The rotational structure has been investigated[107], together with the vibrational structure, of the bands of all three diazines. It is important to note that the 0–0 bands proved to be polarised at right angles to the plane of the azine molecule. Apart from the above bands, a study has been made[108] of weak absorption by pyrazine in the region of 3700 Å.

Studies have been made of absorption at shorter wavelengths of 2000–1500 Å by pyrimidine and pyrazine[96] and by all three diazines[68]. The spectra of pyrimidine, pyridazine, and pyrazine have been found to contain respectively four, two, and three bands—at wavelengths of 1932, 1911, 1777, and 1705; 1940 and 1745; and 1960, 1800, and 1650 Å—while a further band at 2000 Å has been suggested in the case of pyridazine. The absorption spectra of the completely deuteriated diazines have also been investigated[68].

(*b*) Spectra of solutions. Absorption spectra in various polar solvents and in hydrocarbons have been obtained for pyrimidine[103,109], pyridazine[110–112], pyrazine[104], and all three diazines[113,114]. This work relates to the sharp bands in the spectra of the vapours, and the following generalisations can be made. Increase in the concentration of a hydroxylated solvent mixed with a hydrocarbon is accompanied by displacement to shorter wavelengths with the intensity practically unchanged, while the vibrational structure becomes diffuse and the absorption continuous. As the acid concentration increases the absorption of all the diazines gradually disappears.

The bands corresponding to the diffuse bands of the vapours exhibit different properties in solvents: a slight hyperchromic effect is observed, while the positions of the maxima remain practically unchanged (in water and hydroxylated solvents). In acidic solvents there is a strong

hyperchromic effect, a bathochromic effect in the case of pyrazine and a hypsochromic effect with the other diazines. A two-step pH variation in ϵ_{max} has been found[115-117] (for all the diazines).

(*c*) Absorption and phosphorescence at low temperatures. The luminescence of pyrazine was first observed[58] in EPA mixture† at 77°K and the corresponding absorption in isopentane at 293°K in the region of 26 000 cm^{-1} with the one progression $\Delta\nu = 606$ cm^{-1}. A more detailed study of the phosphorescence of pyrazine has been made[59] at 90°K in many solvents. From their effect on the spectrum these can be divided into two groups: in EPA, ethanol, and petroleum ether the bands are diffuse in character, whereas in crystalline matrices of carbon tetrachloride, cyclohexane, dioxan, and benzene the bands possess a sharply defined line structure. Analogous investigations have been made[54] on pyrimidine. Other studies have been made[118,119] of the phosphorescence of pyrazine and pyrimidine. An investigation of the phosphorescence of all three diazines showed[120] that pyridazine does not phosphoresce at all.

Polarisation measurements made by the photoselection method[121] have established[122-124] that the phosphorescence of pyrimidine and pyrazine is polarised along the x and y axes respectively (Table 2).

It has been found[125,126] that transitions forbidden by the selection rules are intensified in the absorption of all three diazines in crystals of hydrogen, neon, argon, krypton, and xenon at 4.2°K.

3. 1,3,5-Triazine

Two band systems—sharp and diffuse, with maxima at 36 780 and 45 000 cm^{-1}—have been observed[127] in the absorption spectrum of 1,3,5-triazine vapour. Dissolution in acetonitrile, methanol, and water displaces the maximum of the first band by 520, 670, and 1670 cm^{-1} respectively to shorter wavelengths compared with the solution in cyclohexane, while the maximum of the second band does not move. The vibrational structure of the first band has been analysed[128]. It was established from the rotational structure that the permitted electronic transition corresponds to polarisation perpendicular to the plane of the molecule. Besides absorption, phosphorescence has been observed[129] in EPA solution at 77°K, as a band with its origin at 26 400 cm^{-1}. This work also revealed absorption in the range 13 000–31 000 cm^{-1}, which had not been noted in the earlier work[127].

4. 1,2,4,5-Tetrazine

Symmetrical tetrazine is characterised by absorption in the visible region with a pink colour[130-133]. A detailed investigation of the absorption spectrum over a wide range, 15 000–45 000 cm^{-1} (6000–2200 Å), has shown[134] the presence of strong absorption with a maximum at 2520 Å and a shoulder at 3200 Å, together with a sharp band system in the region of 18 000 cm^{-1}. In aqueous solution the shoulder and the visible absorption are displaced to shorter wavelengths. Studies have been made[76,77] of the vibrational structure at high resolution in the visible absorption of symmetrical tetrazine and its deuterium analogue (in the vapour state and in solutions). An important result of the rotational analysis[135] of the 0–0 band at 5515 Å was the finding that the molecule has a planar structure in the excited electronic state and that polarisation of the electronic transition is perpendicular to the plane of the molecule. Examination of the fluorescence in various solvents at 77°K and comparison with the absorption spectrum showed a mirror-image relationship between the emission and absorption spectra[136,137]. The vibrational structure becomes blurred on passing to solvents in which hydrogen bonding occurs, and the fluorescence undergoes an anomalous shift to longer wavelengths, in contrast to the opposite shift in the absorption.

Combined data will be found[114,138] on frequencies and wavelengths of the 0–0 bands, the band maxima, oscillator strengths, and molar absorption coefficients in the spectra of all azines and many of their derivatives in various solvents. All the most important experimental spectral data for the azines are given in Table 4.

B. THEORETICAL WORK ON ABSORPTION AND EMISSION SPECTRA

1. Comparative Characteristics of $\pi-\pi^*$ and $n-\pi^*$ Transitions

The old problem of the interrelationship between the absorption spectra of molecules and their structure is soluble in principle by quantum mechanics. The subdivision of electrons in a molecule into σ- and π-electrons has enabled regions corresponding to optical transitions of these electrons ($\sigma-\sigma^*$ and $\pi-\pi^*$ transitions, both denoted $N\rightarrow V$) to be delineated in the absorption spectra of hydrocarbons. In the case of aromatic systems containing heteroatoms, transitions of the lone-pair electrons to vacant σ^*- and π^*-orbitals ($n-\sigma^*$ and $n-\pi^*$ transitions, both denoted $N\rightarrow Q$) must also be taken into account. Since transitions of types $\pi-\pi^*$ and $n-\pi^*$ correspond to the same spectral region, the problem arises of establishing criteria by which they can be distinguished. The comparative characteristics of transitions of the two types are listed in Table 5, which is based on Refs. 139–142 and an analysis of experimental results. We will briefly clarify the main generalisations in this table.

Since an $n-\pi^*$ transition involves passage of the electron from a non-bonding orbital to an antibonding π^*-orbital, and a $\pi-\pi^*$ transition occurs from a bonding orbital to the same antibonding orbital, the former transitions will correspond to longer wavelengths. The low intensities of $n-\pi^*$ transitions are explained by the fact that only the $2s$-function of the hybrid orbital of the n-electron, which weakly overlaps the p-function of the upper state, makes a contribution to the transition dipole moment[140]. The polarisation properties are determined by the symmetry of the orbitals in the lower states of transitions of both types: n-orbitals are symmetric, while π-orbitals are antisymmetric, with respect to the plane of the molecule.

In a hydroxylated solvent conditions are created for the formation of hydrogen bonds of the type N...H–O, which stabilise the lone pair of electrons and therefore produce a

† A solvent comprising 5 parts of diethyl ether, 5 parts of isopentane, and 2 parts of ethanol by volume—cf. G.H.Lewis and D.Lipkin, J. Amer. Chem. Soc., 64, 2801 (1942) (Ed. of Translation).

TABLE 5. Comparison of chief characteristics of $n-\pi^*$ and $\pi-\pi^*$ transitions in the spectra of azines.

Band characteristics	$n-\pi^*$ Transitions	$\pi-\pi^*$ Transitions
Wavelength (for the first transitions)	2700–5500 Å	2500 Å
Molar extinction coefficient	300–1000	1000–6000 (except for 1,3,5-triazine)
Polarisation of absorption for singlet–singlet transitions	Allowed transitions polarised perpendicular to the plane of the molecule	Allowed transitions polarised in the plane of the molecule
Effect of a polar solvent (compared with the spectrum in a hydrocarbon) (*a*) alcohols and water	Hypsochromic shifts without substantial change in intensities; position of maximum depends on concentration of hydroxyl-containing solvent	Effect insignificant
(*b*) acid	Gradual weakening of absorption, until it disappears as the acid concentration increases	Always a hyperchromic effect, the intensity depending on the acid concentration; the magnitude and direction of the shift depend on the compound
Vibrational structure	Very sharp in vapour and crystals, less sharp in hydrocarbon, and becomes indiscernible in polar solvents	Diffuse
Vibrational progressions	The main frequencies forming progressions are those of totally symmetric deformation vibrations of the ring	Frequencies of totally symmetric stretching vibrations are involved
Envelopes of electronic–vibrational bands	They possess atomic sharpness; rotational structure resolved	Diffuse
Shift on conjugating substitution	Hypsochromic	Bathochromic

hypsochromic effect. This view is supported by measurements [112,143] indicating that the energy represented by the displacement of the absorption band for pyridazine and the energy of the hydrogen bond are equal. The band maximum shifts with increasing concentration of the solvent, and this has been used to investigate complex formation. Hydrogen bonding is concerned in the explanation of the hypsochromic shift based on the Franck–Condon principle [118,119].

In acid solution protonation occurs, accompanied by a strong hypsochromic shift in the $n-\pi^*$ transition. With increasing acid concentration, therefore, the gradual "disappearance" of the band is observed in the region examined. Calculation shows [144,145] that protonation changes the field of the skeleton and increases the oscillator strength of $\pi-\pi^*$ transitions, whereas the direction of displacement of the band depends on the nature of the solute and differs for the various azines. Hydrogen bonding or protonation leads to a broadening of the vibrational bands and a diffuse character of the vibrational structure of the transition.

Doubt has been cast [146] on the method of differentiating between $n-\pi^*$ and $\pi-\pi^*$ transitions based on the comparative characteristics described above. It is stated that the observed changes in the spectra produced by a solvent can be explained not only by local interactions between the two molecules but also by the general influence of the internal field in a liquid. A rather more conclusive method is therefore proposed for detecting $n-\pi^*$ transitions, based on hydrogen-bond formation in a non-polar solvent. For this purpose a small amount (0.01 M) of a feebly dissociated acid is added to a solution of the azine in a hydrocarbon. The $n-\pi^*$ transitions in the spectra of azines dissolved in hexane were investigated [146] in the presence of acetic acid, methanol, and phenol. A solution containing no proton-donor was taken as zero for the readings. An advantage of the method is that the concentration of the chromophore is not limited, and the investigation is made in the range of validity of the Lambert–Beer law.

After the bands observed experimentally in the spectra of azines have been assigned, the problem arises of a quantitative theoretical determination of the frequencies and intensities of transitions, with their classification on the basis of the symmetry properties of the molecules. This problem is solved by the three main methods of quantum chemistry—valence pairs, molecular orbital, and free electron methods—using group theory.

2. Calculation of Excited Electronic States and Main Parameters of Electronic Transitions

(*a*) $\pi-\pi^*$ Transitions. Present-day calculations can be subdivided into simplified calculations, in which the transition energy is determined as the energy of excitation of one electron, and more exact calculations, in which the wave function of a molecule is built up as an antisymmetrised product of molecular-orbital and spin functions, the interaction of the electrons and their configurations being taken into account.

The first type includes calculations by the sample Hückel method, which have been made for pyridine [95,147] and for all the azines [148,149]. In the last of these [149] second-order perturbation theory was included within the framework of the simple molecular-orbital method. The calculation has been made also for symmetrical tetrazine [150]. All such calculations are semi-empirical in character, and enable only the position of the absorption band of longest wavelength to be predicted. Only one paper [149] has compared the positions of such bands in a series of azines. Another variant of the same one-electron approximation is the free-electron model, in which the role of the heteroatom is allowed for by introducing an additional potential well near it. A particularly large number of such calculations have been made for pyridine [151–155]. The last of these papers includes a calculation of the energy of the first transition in pyrimidine. In another case [156] σ-potentials were introduced for the nitrogen atom in pyridine, pyrazine, and 1,3,5-triazine. A somewhat modified form of the method has been applied to pyridine and pyrazine [157]. The possibilities of all such calculations are confined to computation of the wavelength of the first band, while greater errors are involved in determination of oscillator strengths, and singlet and triplet states are not distinguished with respect to energy.

A far more complete description of the spectra is obtained by more exact methods. In the first, widely known attempt of this type [158] the various integrals were estimated by a semi-empirical method, and calculations made of the positions of singlet and triplet levels, oscillator strengths, and also bond orders in pyridine, pyrimidine, pyrazine, and 1,3,5-triazine. A detailed analysis has been made [159] of Pariser and Parr's method [158]. An analogous calculation for 1,2,4,5-tetrazine allowed for configuration interaction [160,161]. These last calculations, however, gave an unsatisfactory result owing to an unfortunate choice of orbitals for the initial approximation, although the resonance integral of the nitrogen–nitrogen bond calculated in this work (−2.35 eV) became generally accepted.

At a further stage calculations were made by the self-consistent field (Pariser–Parr–Pople) method[162], using the Pople approximation[163] for the Hartree–Fock Hamiltonian, together with a semi-empirical estimate of various integrals[158]. These calculations were made[164-166] with the separation of a term common to all the azines, and representing the electron affinity of the nitrogen atom, in the coulombic integral at the atom. With a single choice for this parameter it was possible to predict satisfactorily four excited singlet states for all the azines other than symmetrical tetrazine. The best results in calculating the energies of excited states are achieved[167] by using self-consistent orbitals including a limited number of configuration interactions. Calculations of the same type, but with a somewhat different estimate of the electronic interaction integrals, were made for pyridine, pyrazine, and 1,3,5-triazine[168,169] and for 1,2,4,5-tetrazine[170]. The same method has been used[171] in calculations for all the azines other than symmetrical tetrazine. However, agreement with experimental values for the transition frequencies proved unsatisfactory. The best results for all the azines (singlet and triplet states, oscillator strengths) were obtained[172] by taking into account the dependence of the resonance integrals on the bond lengths in the series of azines (these results are given in Table 4).

Analysis of all the calculations listed above leads to the conclusions that the electronic configurations between which significant interaction occurs are of the same type in benzene and in the azines. A parallel classification of electronic transitions in the spectra of these molecules is therefore possible.

Calculation by the self-consistent field method, with interaction of the electrons taken into account, does not ensure a sufficiently exact description of excited states. Such a description is considerably improved by allowing for configuration interactions, the most important of which are those corresponding to transitions from two filled upper orbitals to two vacant lower orbitals. A good interpretation of the electronic spectra is then achieved.

With regard to the vibrational structure of $\pi-\pi^*$ transitions, the angles retain their equilibrium values on excitation of a π-electron, while the bonds become only slightly longer. In conformity with the Franck–Condon principle, therefore, the frequencies of totally symmetric stretching vibrations in the excited state should be the most intense[173]. Experiment confirms this conclusion: progressions with the frequencies of totally symmetric stretching vibrations are observed in the absorption spectra of pyridine[93] and the diazines[68,106] in the region of 1550–2000 and 2500 Å.[68]

(*b*) $n-\pi^*$ Transitions. A more fundamental rearrangement of the whole electron shell of the molecule is produced by this transition. The nitrogen atom acquires a positive charge, while a seventh electron appears in the π-electron system. In the excited state, therefore, the properties of the hybridised functions[174] of the nitrogen atom are changed, while the change in the skeleton affects also the π^*-electron functions. These changes complicate the calculations, which are less satisfactory in the case of $n-\pi^*$ transitions.

A simplified model, in which the interaction between a pentadienyl radical and a nitrogen atom having two *p*-electrons is considered, has been used[175] to calculate the energy of the first $n-\pi^*$ transition in pyridine. Since delocalisation of the seventh electron was ignored, the calculation proved unsatisfactory.

An extended form of the Pariser–Parr method, in which the n-electrons were explicitly allowed for in calculating the atomic integrals, was used in a series of papers[176-179]. The energies of the singlet and triplet states of pyrimidine and pyrazine were calculated. However, a satisfactory result was obtained only on the assumption that the 2*s*-function participated to a small extent in hybridisation, in both ground and excited states. But this hypothesis leads to difficulties in explaining the valency angles in the ground state and the intensities of the transitions[174]. The hybridisation parameter was not calculated theoretically, but merely estimated from spectroscopic data.

This defect is absent in calculations[180], without variation of the hybridisation parameter, of the singlet and singlet–triplet transition energies in pyridine, pyridazine, and pyrimidine. The energy of the ground state was determined as the sum of the energies of six π-electrons in the field of the nuclei and the energy of one electron in a doubly occupied orbital, whereas the energy of the excited state was regarded as the energy of seven electrons in the field of the skeleton with a double positive charge on the nitrogen atom. Various integrals on which the difference between these energies depends were computed[180]. But the calculation made it possible to find only mean values of singlet and triplet states. These states could then be separated by application of a method[181] taking into account exchange interactions.

Nevertheless, the most complete description of the spectra of all the azines was accomplished by means of semi-empirical calculations to the one-electron approximation[114,174,182]. These papers showed that the energy of $n-\pi^*$ transitions was determined by two factors—the fall in the energy of the molecular orbitals of the π^*-electrons on introduction of the heteroatom, and the interaction between n-electrons in different atoms—the first factor being due to the enhanced electronegativity of the nitrogen atom relative to carbon, and the second being most significant in the presence of adjacent nitrogen atoms. When these factors were taken into account, the shifts in the $n-\pi$ bands relative to pyridine could be explained throughout the series of azines.

1,3,5-Triazine is especially interesting, since in this molecule the highest filled n-orbitals and the lowest vacant π^*-orbitals are degenerate. Allowance for the configurational interaction eliminates this degeneracy. Calculation of the removal of degeneracy revealed[183] that the resolution is small (around 1 eV) with various sets of semi-empirical values for the integrals, while all transitions between sublevels lie within the same band at 3200 Å.

The oscillator strengths f vary in the series of azines (see Table 4). These changes have been explained[174] by changes in the degree of delocalisation of the π-orbitals and differences in configuration interactions, which play an important part in the calculation of f. Accompanying calculations[174] of differences in energy between singlet and triplet states yielded reasonable values only on the assumption of a small participation of 2*s*-functions in the hybrid functions of the excited states. The above calculations determine the positions of excited singlet and triplet energy levels in azines, which are required in order to explain both absorption and emission spectra. However, the latter exhibit specific regularities. Among all the azines[137] only 1,2,4,5-tetrazine fluoresces, whereas pyrimidine and pyrazine exhibit intense phosphorescence. Pyridine and pyridazine do not luminesce at all. The reasons for these phenomena have been cleared up[184]. The lowest excited

singlet state in azines is an $S(n,\pi^*)$ state. The probability of a transition from it to the ground state is very small. But this is not the main reason for the absence of fluorescence. The main competing process suppressing it is a radiationless transition from the $S(n,\pi^*)$ state to a triplet state $T(\pi,\pi^*)$, located below the former state. This follows from a calculation of the probability of such a transition, which becomes possible as a result of spin–orbital interaction. Such a transition does not occur in symmetrical tetrazine, since the $T(\pi,\pi^*)$ level is located above the $S(n,\pi)$ level, and this compound therefore fluoresces. Phosphorescence is due to an intersystem transition from the $T(n,\pi^*)$ state to the ground state. Such a transition, however, may be radiationless. It is supposed [184] that in pyridine and pyridazine the probability of this process is high. But this explanation does not settle the problem, since this probability has not been determined, and the reason for the phosphorescence of pyrimidine and pyrazine remains obscure.

C. PRINCIPLES OF THE CLASSIFICATION OF ELECTRONIC STATES AND THE INTERPRETATION OF ELECTRONIC SPECTRA

Group theory provides the most general method for classifying electronic energy levels. The symmetry type of each electronic configuration is determined as the direct product of the symmetry types of molecular orbitals filled with one or two electrons. The ground state of the molecule is totally symmetric. When configuration interaction is taken into account, two cases must be distinguished: if the interacting configurations are not degenerate, the resultant state possesses the symmetry of the individual configuration (only configurations of the same symmetry type interact); if, however, one or more interacting configurations are degenerate, several states of different symmetry types arise. The notation for the excited states and transitions is identical with that of the symmetry types.

The second method is applied especially to cyclic systems containing conjugated bonds [185]: the one-electron energy levels are classified according to the values of the projection m_q of the angular momentum on an axis perpendicular to the plane of the molecule. If the sum of the m_q over all electrons in the molecule is 0, ±1, ±2, ±3, the states are denoted for monocyclic systems by A, B, C, L. A state having $\Sigma m_q \neq 0$ is doubly degenerate. The presence of a heteroatom eliminates the degeneracy, and the components of the splitting are denoted by Ba, Bb, Ca, Cb, La, Lb. A one-to-one correspondence is stated [186] to exist between the notations of the two methods, which are indicated in Table 4. Finally, the purely empirical notation—α, p, β, β'—was introduced [187] for transitions from the ground state to the states ^1L_b, ^1L_a, ^1B_b, and ^1B_a. The applicability of this notation to azines has been justified [164,167] by comparing the energy levels and the spectra of the azines and benzene. All these symbols are applicable only to $\pi-\pi^*$ transitions. Only the symbols of group theory are to be used for $n-\pi^*$ transitions, since the properties of n-electrons are not in general represented by the model of free electrons on which the notation of Ref. 185 was based.

The symbols of the transitions are closely linked with their polarisation properties. For singlet–singlet transitions the polarisation is unambiguously defined by the symbol of the upper state and the symmetry types of Cartesian coordinates. To establish the polarisation of a singlet–triplet transition it is necessary to know the symmetry of the sublevels into which the triplet level splits as a result of spin–orbit interaction. Such determinations have been made for the azines [188].

Interpretation of Electronic Spectra

Analysis of the above experimental and theoretical work enables a complete interpretation to be given for the absorption and luminescence spectra of the azines. The absorption spectra are set out in Table 4, in which columns 3–13 give the main characteristics of the $\pi-\pi^*$ transitions, and columns 14–18 those of the $n-\pi^*$ transitions. Assignment of the former transitions was based on the correspondence between the spectra of the azines and that of benzene. Theory predicts for pyridine and the diazines two transitions each in the range 1600–1700 Å. Only one maximum is observed experimentally in this range, which is consistent with the small degree of resolution of the benzene band at 1790 Å. The La-bands correspond to the benzene band at 2050 Å. They show a marked discrepancy between calculated and measured oscillator strengths, which may be tentatively explained by superimposition of a $\sigma-\pi^*$ transition in the same region. The Lb-bands correspond to the benzene band at 2600 Å, and are less intense than the B-bands.

As early as 1954 [127] all the long-wavelength sharp band systems were assigned to $n-\pi^*$ transitions on the basis of a study of solvent effects. Analysis of the rotational structure of corresponding 0–0 bands of diazines [107], 1,3,5-triazine [128], and 1,2,4,5-tetrazine [135] showed them to be polarised perpendicularly to the plane of the molecule. This fact finally confirms the assignment of the transitions to the $n-\pi^*$ type. Table 4 shows very clearly the effects of solvents on transitions of both types.

It follows from the scheme of energy levels [174] that a second permitted $n-\pi^*$ transition occurs in pyrimidine, pyridazine, and symmetrical tetrazine. To such transitions have been assigned the bands at 1932 and 1942 Å in pyrimidine and pyridazine [68] and at 3200 Å in 1,2,4,5-tetrazine [134]. The positions of the bands agree with theoretical predictions [174], but their assignment is tentative, and they are not included in Table 4.

While Table 4 indicates only singlet–singlet transitions, the singlet–triplet transitions are given in Table 6. [174] The latter are assigned to intersystem transitions in view of the long life-time of the excited states and the small oscillator strengths [174,188]. The important part played by radiationless transitions from excited states of the molecules was already pointed out in the early work [139,140]. In most cases, therefore, the nature of the radiating transition ($\pi-\pi^*$ or $n-\pi^*$) is determined by the type of the lower excited state, and the type of phosphorescence depends on the relative positions of the $T(\pi,\pi^*)$ and $T(n,\pi^*)$ levels [189]. Theoretical calculation is not a reliable criterion, since these states may be very close together, and the distinguishing features listed in Table 5 are used to assign the $S-T$ transitions.

The symmetry types indicated in Table 6 have been established from the correspondence with absorption bands and the law of mirror symmetry. Symmetrical triazine forms an exception. The long life-time indicates that the transition is forbidden not only with respect to spin but also with respect to symmetry. The transition is therefore assigned not to $^3A_2''$ but tentatively [174] to $^3E''$. Table 6

TABLE 6. Intersystem transitions in azines.

Compound	Position of 0–0 band, Å: absorption	Position of 0–0 band, Å: phosphorescence	Life, s	Assignment and polarisation
Pyridine	3381	—	—	$^3A_1(\pi, \pi^*)$
Pyrimidine	—	3534		$^3B_2(n, \pi^*)$, x
Pyrazine	3765	3769	$2\cdot10^{-3}$	$^3B_{1u}(n, \pi^*)$, y
1,3,5-Triazine	(3846)	(3788)	0.46	$^3E''(n, \pi^*)$

does not include the luminescence of symmetrical tetrazine, since the band at 5571 Å is assigned, in view of the short life-time and on the basis of the law of mirror symmetry, to the singlet–singlet transition $^1B_{1u}$: i.e. it is fluorescent.

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GAS CHROMATOGRAPHY WITH TEMPERATURE PROGRAMMING

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1. INTRODUCTION

The gas-chromatographic analysis of complicated mixtures of organic compounds, differing markedly in partition coefficients, almost always requires the application of a variable temperature. In fact, it is impossible to choose a constant temperature such that light and heavy components can be separated satisfactorily in the same analysis. If a low temperature is chosen, light components will be separated satisfactorily, but a long time will be required to analyse the heavy components. Furthermore, because of the considerable spreading of the peaks, the sensitivity of the chromatograph will be too low for the heavy components. At a high temperature the heavy components readily show up, but the retention time of the light components is so short that they cannot be separated even on a highly efficient column.

The problem has been solved by applying to the mixture to be separated either a moving temperature profile with a constant temperature gradient in the direction of flow of the carrier gas, or by varying the temperature simultaneously along the whole column.

The former method was proposed and developed by Zhukhovitskii and Turkel'taub together with their collaborators [1-5], and is termed stationary chromathermography. In this method the components of the mixture are distributed inside the column in such a way that the less volatile substances are located near the inlet, where the temperature is higher, and the more volatile substances near the outlet. The components remain practically stationary relative to the furnace producing the temperature gradient, and move towards the outlet from the column at the same speed as the furnace gradient. In the course of time the bands shrink and the mixture becomes enriched.

The other method, which has been called the programmed temperature method, was proposed by Griffiths et al. [6] Temperature programming permits the light components to escape at low temperatures, and the heavy components at high temperatures. In this way an acceptable retention time is obtained, together with quite narrow peaks for both light and heavy components.

At the present time the temperature programming method, which is simpler in practice, is predominantly used, and most of the papers have been devoted to it. Undoubtedly the stationary chromathermography method also shows promise, and will be developed in the future. The present paper discusses only the temperature programming method. A detailed description of stationary chromathermography can be found in two monographs [7,8].

The practice of temperature programming has developed greatly. A theory has been constructed which enables results for isothermal chromatography to be used to determine the retention temperature, ascertain the degree of component separation as a function of the operating conditions, and identify the components of a complex mixture.

Temperature programming is employed in the quantitative analysis of hydrocarbons, alcohols, ethers and esters, aliphatic acids, aromatic compounds, synthetic oils, etc.[9-16] Both packed and capillary columns are used. Several firms market instruments for chromatography with temperature programming.

Temperature programming in gas chromatography usually involves the use of linear programmes of the type

$$T = T_0 + rt \tag{1}$$

where T_0 is the initial temperature, r a parameter characterising the rate of change of temperature, and t the time. The choice of linear programmes is dictated primarily by the simplicity of producing them. But the most important reason is that linear programming enables reliable results to be obtained in the quantitative analysis of multicomponent mixtures. The peaks of components belonging to the same homologous series emerge at approximately equal intervals of time in a linear programme, while the resolution of the components is almost the same as under isothermal conditions. However, special forms of nonlinear programmes have several advantages, which will be discussed at the end of this paper.

2. DETERMINATION OF RETENTION TEMPERATURE AND TIME IN LINEAR PROGRAMMING

Underlying the theory of programmed-temperature gas chromatography is a simple equation obtained by several workers[17-20]. If a chromatographic peak traverses a path dl at a speed v in time dt, we have the differential equation

$$dl = v\,dt. \tag{2}$$

At constant temperature Eqn. (2) can be integrated to give

$$L = vt_R \tag{3}$$

where L is the length of the column and t_R the retention time of the peak. On the other hand, the retention time can be expressed in terms of the retention volume V_R and the speed of the carrier gas u:

$$t_R = \frac{V_R}{u}. \tag{4}$$

At any temperature the speed v of the peak at a given instant is

$$v = \frac{uL}{V_R} \tag{5}$$

(if u and V_R are measured at the same mean pressure in the column or at the pressure at the outlet). Substituting from Eqn. (5) in (2), we obtain

$$dl = \frac{uL}{V_R}\,dt. \tag{6}$$

Integration of Eqn. (6) yields

$$\int_0^{t_R} \frac{u\,dt}{V_R} = 1. \tag{7}$$

If the temperature is assumed to vary linearly with time as in Eqn. (1), we find that Eqn. (7) becomes

$$\int_{T_0}^{T} \frac{u}{r}\,\frac{dT}{V_R} = 1. \tag{8}$$

If there is a controlled rate of flow, and this rate is independent of temperature, it follows from Eqn. (8) that

$$\int_{T_0}^{T} \frac{dT}{V_R} = \frac{r}{u}. \tag{9}$$

Eqn. (9) is the starting point for further analysis. It is interesting in that the integral on the left-hand side is the same for all components and columns: it is determined solely by the rate r at which the temperature rises and the speed u of the carrier gas.

The retention volume V_R should be corrected for expansion of the carrier gas. Correction factors, which depend on the pressure gradient in the column, have been given in Ref. 21.

The corrected retention volume can be written

$$V_R = V_m + V_R' \tag{10}$$

where V_m is the retention volume of the gas peak, and

$$V_R' = Ae^{\frac{\Delta H}{R_0 T}}. \tag{11}$$

Eqn. (11) gives the temperature dependence of the retention volume. Here ΔH is the heat of dissolution, R_0 the universal gas constant, T the absolute temperature, and A a constant independent of temperature.

Eqn. (9) can be generalised by making it independent of column length for a column of a given type[22]. On multiplying both sides of this equation by m, the quantity of liquid phase present in the column, we obtain

$$\int_{T_0}^{T} \frac{dT}{V_{Rg}} = \frac{r}{F} \tag{12}$$

where $V_{Rg} = V_g + V_m/m$ is the retention volume per unit mass of the liquid phase, and $F = u/m$ is the speed of the carrier gas per unit mass of the liquid phase.

If, in particular, the length of the column is doubled, while the speed u of the carrier gas remains unchanged, F will be halved, and the retention temperature, i.e. the temperature at which a peak appears, will be given by

$$\int_{T_0}^{T} \frac{dT}{V_{Rg}} = \frac{2r}{F}. \tag{13}$$

But if, at the same time as the column length is doubled, r is halved or u is doubled, the retention temperature will be unchanged.

Eqn. (7) and hence Eqn. (9) can be simplified by postulating that the speed of a peak due to a component is small at $T \simeq T_0$, and that heating is started at the instant of appearance of the carrier-gas peak. We then have

$$\int_{t_a}^{t_R} \frac{u}{V_R'}\,dt = 1 \tag{14}$$

and

$$\int_{T_a}^{T_R} \frac{dT}{V_R'} = \frac{r}{u}, \tag{15}$$

in which t_a is the retention time for the carrier-gas peak, T_a is its retention temperature, and V_R' is defined by Eqn. (11). Rowan considers[20] that Eqn. (15) is accurate, but actually this is not so. If the retention volume of the carrier-gas peak is large (e.g. in a capillary column), the error will be considerable.

Eqn. (9) has several times been tested experimentally. For example, Rowan[20] made a careful comparison of theoretical values of the retention temperature with experimental results. From Eqns. (15) and (11) he obtains for the elution temperature of the components the expression

$$\frac{rAR_0}{u\Delta H}=\int_{\Phi_1}^{\Phi_2}-\frac{e^{-\Phi}}{\Phi^2}d\Phi \qquad (16)$$

where

$$\Phi=\frac{\Delta H}{R_0T},\ \Phi_1=\frac{\Delta H}{R_0T_a},\ \text{and}\ \Phi_2=\frac{\Delta H}{R_0T_R}. \qquad (17)$$

Integration by parts yields

$$\frac{rAR_0}{u\Delta H}=\left[\frac{e^{-\Phi_2}}{\Phi_2}-\frac{e^{-\Phi_1}}{\Phi_1}+\int_{\Phi_1}^{\Phi_2}\frac{e^{-\Phi}}{\Phi}d\Phi\right]=f(\Phi_1-\Phi_2;\Phi_1) \qquad (18)$$

in which all quantities other than Φ_2 and hence T_R are known (A and ΔH are determined from isothermal data). The paper contains tables, compiled by the author, of values of the function f for various values of $\Phi_1-\Phi_2$ and Φ_1. By plotting graphs of this function $f(\Phi_1-\Phi_2,\Phi_1)$, it is easy to determine Φ_2 and T_R for known values of A, ΔH, r, and u. The good agreement with experiment justifies the use of Eqn. (15) as starting point for further calculations.

Measurements have been made[22] of retention volumes in a capillary column for 2,3,3- and 2,3,4-trimethylpentane as a function of temperature in isothermal processes. From these data, the integral

$$\int_{T_0}^{T}\frac{dT}{V_{Rg}} \qquad (19)$$

was evaluated as a function of T_R by numerical integration, and hence the retention temperature was calculated for various values of r/F (from 0 to 0.07 g cm^{-3}). Here, too, agreement between theoretical values and experimental results was good.

In both these[20,22] and other papers the calculated retention temperature was lower by several degrees than the experimental values, and this difference increases with increase in the rate of heating r of the column. Giddings has shown[23] that these errors are caused by a temperature gradient between the walls and the centre of the column. This gradient is due to thermal inertia, and the column therefore operates at lower temperatures than are assumed in the calculations. At the same time the temperature gradient inside the column causes additional spreading of the peaks, which somewhat impairs the separation of the mixture. Temperature distribution profiles in the column have been calculated[24] for various rates of heating.

Dal Nogare and Langlois[18] and Giddings[19] have attempted to calculate the velocity of the peak due to a component by means of the refined formula (11) for the retention volume, with the coefficient A evaluated as a function of the column parameters. The formulae obtained were extremely complicated. In particular, the linear relation between retention time and number of carbon atoms in molecules of a homologous series was shown only by numerical integration on a computer[18]. In order to obtain retention times or temperatures in these papers, the chief constants had to be determined empirically from isothermal chromatographic data, as in other papers[17,20,22]. A detailed account of this work[18,19] has been given in a review by Vigdergauz and Gol'bert[25]. Therefore we shall not discuss it further, especially as application of the simple formula (11) has been shown by several workers to yield good results.

Another paper by Rowan[26] mentions a method for determining the elution temperature of a component when the pressure remains constant at the outlet and the inlet of the column. The speed of the carrier gas then varies according to the law

$$u=\frac{M}{T}+N \qquad (20)$$

where M and N are constants. This paper contains tables and graphs for calculating the retention temperature T_R. In programmed-temperature gas chromatography, however, a constant flow of the carrier gas is usually established, not a constant pressure. It is not necessary, therefore, to discuss the paper[26] in detail.

3. THE EQUIVALENT TEMPERATURE

The so-called equivalent temperature T_r —the constant temperature at which a peak is eluted in the same time as with the programmed temperature—is of considerable interest. It obviously lies between the limits $T_0<T_r<T_R$. The concept of "equivalent temperature" was introduced by Giddings[27,28].

The time t for elution of a peak at a constant temperature T_r is

$$t=\frac{V_{T_r}}{u} \qquad (21)$$

where V_{T_r} is the retention volume at this temperature. On the other hand, the elution time of a peak with a programmed temperature is

$$t=\frac{T_R-T_0}{r}. \qquad (22)$$

Equating (21) and (22), we obtain

$$r=\frac{u(T_R-T_0)}{V_{T_r}}. \qquad (23)$$

Substitution for r in Eqn. (9), with the speed of the carrier gas assumed constant, yields the equation

$$\int_{T_0}^{T_R}\frac{dT}{V_R}=\frac{T_R-T_0}{V_{T_r}}, \qquad (24)$$

which relates T_R with T_r, since V_{T_r} depends on the latter temperature.

To find the approximate dependence of T_r on T_R we shall neglect the retention volume of the gas peak, i.e. assume that $V_R\simeq V_R'$ and $V_{T_r}\simeq V_{T_r}'$. On then differentiating both sides of Eqn. (24) with respect to T_R, and making certain straightforward rearrangements, we obtain the differential equation

$$\exp\left\{-\frac{\Delta H}{R_0T_R}\left(1-\frac{T_R}{T_r}\right)\right\}=(T_R-T_0)\frac{\Delta H}{R_0T_r^2}\frac{dT_r}{dT_R}+1. \qquad (25)$$

An approximate solution of this equation with $T_0\simeq 300°K$ is

$$T_r\simeq\frac{T_R}{1+0.85\frac{R_0T_R}{\Delta H}}. \qquad (26)$$

With temperature programming the peak usually appears at $T_R\simeq T_k$, the boiling point of the component[29]. The value of the universal gas constant is $R_0\simeq 2$ cal deg^{-1}

mole^{-1}, and we also have the approximate value $\Delta H/T_k \simeq$ 23 cal deg^{-1} mole^{-1}. On the assumption that the boiling point of the component is $T_k \simeq 500°K$, we obtain

$$T_r \simeq 0.9T_R \tag{27}$$

whence

$$T_R \simeq T_r + 50. \tag{28}$$

The mean speed of a sample in a column with temperature programming approximately equals the speed of the sample at a constant temperature 50 deg lower than the temperature at which the peak appears with temperature programming.

4. SHARPNESS OF SEPARATION (RESOLUTION) OF COMPONENTS

The quality of the separation of two neighbouring peaks is usually represented by the expression

$$R = \frac{2(t_{R_2} - t_{R_1})}{W_1 + W_2} \tag{29}$$

where W_1 and W_2 are the widths of the peaks at the base, expressed in terms of time, while t_{R_2} and t_{R_1} are the retention times of the two peaks[22]. The formula (29) is used both in isothermal chromatography and with a programmed temperature. In the case of linear programming we have

$$t_{R_2} - t_{R_1} = \frac{T_{R_2} - T_{R_1}}{r}. \tag{30}$$

According to Habgood and Harris[17] the retention volume V_{T_γ} for a peak at a constant temperature T_γ and the peak width ΔV (retention volume of the peak) with a programmed temperature are linked by the relation

$$n = 16\left(\frac{V_{T_r}}{\Delta V}\right)^2, \tag{31}$$

in which n is the number of theoretical plates in the column, which defines its separating power[30]. The equivalent temperature defined by Eqn. (26) is to be taken[29] as T_γ, not the elution temperature T_R of the peak with temperature programming.

With high rates of heating, when $T_R \gg T_0$, the peak widths remain practically constant at the programmed temperature. It has been shown[31] that the width of a peak is independent of the "previous history" of the warming up of the column.

Since

$$W_1 + W_2 = \frac{\Delta V_1 + \Delta V_2}{F} \tag{32}$$

we obtain from Eqn. (31) the formula†

$$W_1 + W_2 = \frac{4}{F\sqrt{n}}(V_{T_{r_1}} + V_{T_{r_2}}). \tag{33}$$

It is assumed here that the column has the same separating power for the two components.

It follows from Eqns. (29), (30), and (33) that

$$R = 2\frac{F}{r}\frac{T_{R_2} - T_{R_1}}{V_{T_{r_1}} + V_{T_{r_2}}} = R_i\frac{\sqrt{n}}{4}. \tag{34}$$

† Here and subsequently we are dealing with specific retention volumes, i.e. volumes per unit mass of the liquid phase.

The quantity R_i is termed the intrinsic resolution. It is that part of the resolution which is independent of the separating power of the column and is determined by the thermodynamic properties of the components. In most cases R_i is a maximum at values of r/F lying within the range 0.001–0.1 g deg cm^{-3}.[32,33]

Experiment shows[15] that the intrinsic resolution R_i varies very little with F if the ratio r/F is maintained constant. This is not consistent with theoretical views, most likely because an isothermal retention volume is substituted in Eqn. (31). It is interesting that in general the intrinsic resolution varies little with r/F.

If we increase the column length L, while leaving the ratio r/F constant, the retention temperature remains unchanged. The resolution, however, increases as $L^{\frac{1}{2}}$, because $n^{\frac{1}{2}} \propto L^{\frac{1}{2}}$. When the input pressure far exceeds the output pressure, the former must be increased as $L^{\frac{1}{2}}$ for the ratio r/F to remain constant when the speed of the carrier gas is unchanged, while r should decrease as $L^{-\frac{3}{2}}$.[22] Consequently the emergence time of the peak (22) increases with $L^{\frac{3}{2}}$ under the above conditions, as in isothermal chromatography.

Since the intrinsic separation is almost independent of F for identical values of the ratio r/F, it is advisable to operate with values of F for which R_i is a maximum with the given r.

The effect of r on the retention time resembles the effect of temperature in isothermal chromatography. The time for elution of the peak decreases with increase in r, approaching a limiting value. Correspondingly, the resolution diminishes somewhat with increase in r, as is immediately evident from the formula (34).

The number of theoretical plates defined by Eqn. (31) may differ markedly from the corresponding number for a constant temperature. Attempts[17,34] to calculate the number of theoretical plates as a function of the column parameters with temperature programming did not yield results showing good agreement with experiment.

It is found experimentally that, with a programmed temperature, the number of theoretical plates varies with r at a fixed rate of flow, diminishing with increase in r. In the case of temperature programming the resolving power is more difficult to predict than in an isothermal process, where it is proportional to $n^{\frac{1}{2}}$. The resolution of components varies both with the number of plates and with R_i, which depends on r/F.

In conclusion it must be emphasised that experiment shows[22] that the resolution which can be achieved with temperature programming is almost the same as, and sometimes even better than, in isothermal chromatography. If, however, the time available for the analysis has been specified, programming the temperature ensures a sharper separation than does the isothermal process, as Zhukhovitskii and Turkel'taub have shown (Ref. 7, p. 150). Furthermore, the enrichment of the components of the mixture, which is associated with the narrowing of the chromatographic peaks in temperature programming, enhances the sensitivity of the instrument, which is extremely important in the analysis of microsamples[31].

5. RETENTION INDEX

The retention index was introduced by Kováts[35,36] as a measure of the retention of a component which would vary

little with the operating conditions of a separating column or its packing. Consequently the retention index can conveniently be used for the identification of the components of a complicated mixture.

In the case of isothermal chromatography the introduction of the retention index is based on a linear variation in the logarithm of the retention volume V_R' with the number of carbon atoms in unbranched-chain hydrocarbons. The retention index varies very slightly—and linearly—with temperature.

In the case of a programmed temperature, introduction of the retention index is based on an approximately linear dependence of the retention temperature on the number of carbon atoms. The retention index is then by definition

$$I = 100\,\frac{T_R(x) - T_R(z)}{T_R(z+1) - T_R(z)} + 100\,z \qquad (35)$$

where $T_R(x)$, $T_R(z)$, and $T_R(z+1)$ are the retention temperatures of the test compound and of hydrocarbon components containing z and $z+1$ carbon atoms. If the relation between the retention temperature and the number of carbon atoms in the molecules were strictly linear, the retention index would simply equal the number of carbon atoms multiplied by 100. Since, however, this relation will not be exactly linear, the index will not coincide with this product, although in several cases it will be close to the latter. The formula (35) for the retention index is convenient, as it can be evaluated directly from a chromatogram without any preliminary calculations.

The retention index (35) is usually equal to the index for the isothermal process conducted at the equivalent temperature[37].

It is significant that, as experiment shows with a programmed temperature, the retention index varies little over quite a wide range—variation in the initial temperature T_0 and in the rate r of rise in temperature—of operating conditions. If, therefore, a component has once been reliably identified, and its retention index is known, unknown components in a complicated mixture can be identified by measuring their retention indices by means of the chromatogram. A detailed examination has been made[38] of the temperature dependence of the retention index both with temperature programming and in isothermal chromatography.

It is difficult to use the retention temperature T_R directly for purposes of identification, since Eqn. (9) cannot be solved explicitly for constant ΔH, which characterises the component. Values of T_R, however, vary markedly with the operating conditions of the chromatographic column.

6. NON-LINEAR TEMPERATURE PROGRAMMING

The application of linear temperature programming, which has been discussed in the preceding paragraphs, involves certain difficulties. The chief of these is the impossibility of obtaining the retention time (or, what amounts to the same, the retention temperature) in a simple analytical form[8]. Recourse must be had either to numerical integration or even to the use of tables of special functions. Further, the coefficient r, representing the rate of change of temperature, cannot, for technical reasons, be varied continuously. Consequently, in order to obtain different rates of change of temperature, a set of programmes must be used.

These disadvantages (mainly the first) can be eliminated by using a special type of non-linear programme[39]. By this means it is possible to obtain practically the same results as with the linear programme, but with a simple analytical expression for the elution time of various components of the mixture. Furthermore, the choice of different initial points on the programme is roughly equivalent to varying the rate of temperature rise in a linear programme.

If the temperature of the column varies with time according to the law

$$T = \frac{T_0}{1 - \beta t} \qquad (36)$$

where β is a constant defining the rate of temperature rise, we obtain from Eqns. (14) and (11) for the retention time t_R the simple expression

$$e^{\varepsilon t_R} = \varepsilon t_{0R} + e^{\varepsilon t_a} \qquad (37)$$

in which

$$\varepsilon = \frac{\Delta H \beta}{R_0 T_0} \qquad (38)$$

and

$$t_{0R} = \frac{A}{u}\, e^{\frac{\Delta H}{R_0 T_0}} \qquad (39)$$

is the retention time of the peak on chromatographing at a constant temperature. If the elution time t_a of the carrier-gas peak is short, taking logarithms in Eqn. (37) yields the following simple formula for the retention time

$$t_R = \frac{1}{\varepsilon} \ln(\varepsilon t_{0R} + 1). \qquad (40)$$

From Eqn. (40) it is easy to show that the condition of equal distances on the chromatogram between peaks due to successive members of a homologous series is approximately satisfied with the temperature programme (36), provided that the number of carbon atoms in the molecules is sufficiently large. This conclusion is supported by experiment. Retention times measured experimentally for normal alkanes agree well with Eqn. (40).

The above non-linear programme (36) is equivalent to a series of successive linear programmes having increasing values of r. But, since the resolution R is only slightly dependent on r, the resolution obtained with the non-linear programme will differ little from that obtained with a linear programme having $r \simeq \beta T_0$. Of course, the peaks due to heavy components will be rather less well resolved, since they appear at high effective values of r.

With non-linear programming it is possible to introduce a retention index just as with linear programming, but the retention temperature must be replaced by the retention time, since it is the latter which depends approximately linearly on the number of carbon atoms. The retention index can be defined

$$I = 100\,\frac{t_R(x) - t_R(z)}{t_R(z+1) - t_R(z)} + 100\,z \qquad (41)$$

where $t_R(x)$, $t_R(z)$, and $t_R(z+1)$ are the retention times of the test compound and of hydrocarbon components containing z and $z+1$ carbon atoms.

Nevertheless, the relation between the retention time and the parameter ϵ characterising the component is so simple that components can be identified directly from the retention time by means of Eqn. (40).

However, it is not always easy to carry out the isothermal experiment (e.g. with mixtures having a wide range of boiling points). A new method was therefore proposed for determining heats of dissolution ΔH and identifying components, based on the use of two non-linear programmes of the type (36) with different rates of temperature rise[40].

If two chromatograms are obtained with rates of temperature rise defined by the parameters β and $\beta' = \alpha\beta$ (where α is a number), the isothermal retention time t_{0R} of the component can be eliminated, and two equations of the type (40) used to obtain the simple expression

$$e^{\epsilon t_R} = \frac{1}{\alpha} e^{\alpha\epsilon t'_R} + e^{\epsilon t_a} - \frac{1}{\alpha} e^{\alpha\epsilon t'_a} \qquad (42)$$

for determining ϵ and hence ΔH, where t_R and t'_R are the retention times of the component for the different programmes, and t_a and t'_a those of the gas peak. It is easy to evaluate ϵ by the graphical solution of Eqn. (42).

Good results have been obtained in a test of this method of determining heats of dissolution using a mixture of primary alcohols, methyl ketones, and hydrocarbons. The heats of dissolution fitted satisfactorily on straight lines representing the homologous series, which permitted reliable identification of the components.

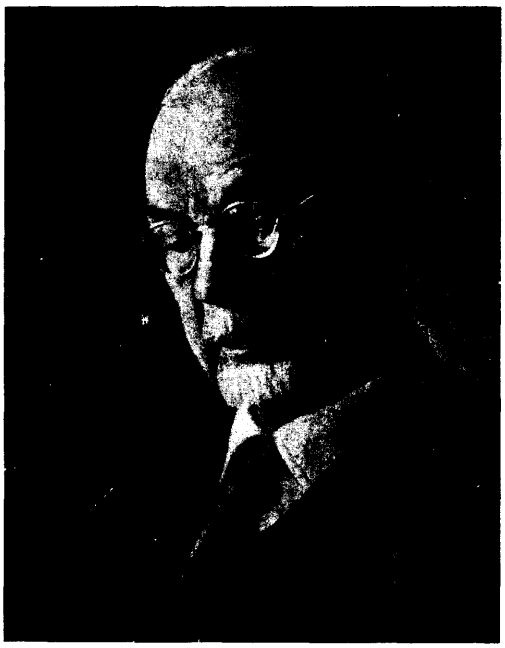
This method of identifying components has the advantage, in comparison with the method based on the retention index, that it does not in principle require a linear dependence of retention temperature on number of carbon atoms. Furthermore, from it an important physical quantity—the heat of dissolution—can be determined.

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RUSSIAN CHEMICAL REVIEWS
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ALEKSANDR ERMININGEL'DOVICH ARBUZOV

Dear Aleksandr Erminingel'dovich!

The Editorial Board of the journal "Uspekhi Khimii" convey to You their heartfelt greetings on the occasion of Your ninetieth birthday and the completion of 65 years of scientific, pedagogical, and public activity.

You are one of the eminent organic chemists of our country, a worthy continuer of the tradition of the great Russian chemists—Zinin, Butlerov, Markovnikov. Your remarkable investigations in the field of theoretical and synthetic organic chemistry and especially the chemistry of organophosphorus compounds have received worldwide recognition. You have created in Kazan' one of the largest schools for studying the chemistry of organophosphorus compounds.

We wish You, dear Aleksandr Erminingel'dovich, good health for many years and new creative successes.

The Editorial Board of the journal "Uspekhi Khimii"

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DEVELOPMENT OF THE CHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS IN THE WORK OF THE KAZAN' SCHOOL OF ORGANOPHOSPHORUS CHEMISTS†

A. N. Pudovik and I. M. Aladzheva

Organophosphorus compounds occupy an important place among the various types of organoelemental compounds in which chemists are now interested. Whilst being extremely interesting theoretically, organophosphorus compounds are also of considerable practical interest. They have found wide application in the various regions of

† Difficulties with nomenclature have arisen in the translation, particularly in the use of the terms phosphinic/phosphonic and phosphinous/phosphonous. These pairs of terms are sometimes used synonymously in the Russian: "phosphonic" can mean phosphinic, phosphonic, or even phosphinic and/or phosphonic. Adjustments have been made where possible to bring the nomenclature in line with current Western practice (Ed. of Translation).

the national economy as pharmaceutical preparations, insecticides and fungicides, plasticisers and stabilisers, surface-active compounds, extractants, catalysts, monomers for the preparation of organo phosphorus fire-resistant polymeric materials, lubricating oil additives, and additives conferring flame-resistance on fabrics, synthetic resins, etc.

The great practical possibilities led to the rapid development of the chemistry of organophosphorus compounds in the last two decades. A large number of new organic derivatives of phosphorus was obtained with the aid of known or new synthetic methods, the problems of the reactivity of the various classes of organo phosphorus compounds were widely studied, and interesting results were obtained appertaining to the structure of these compounds and the mechanism of their reactions.

The Kazan' school of organophosphorus chemists, created and already headed for over half a century by Aleksandr Ermingel'dovich Arbuzov, has played an important part in the development of the chemistry of organophosphorus compounds. In the present review we did not aim at describing all the investigations carried out by the Kazan' chemists in the field of organophosphorus compounds (these studies number more than 700), but have tried to trace the development of the principal scientific directions of the Kazan' school, touching on the study of the conversions of esters and some other derivatives of phosphorus(III) into phosphorus(V) compounds, the addition of organophosphorus compounds with a labile hydrogen atom to compounds with multiple bonds, investigations of the fine structure of organophosphorus compounds by physical and physicochemical methods, the preparation of phosphorus-containing insecticides and physiologically active compounds, the production of phosphorus-containing monomers and polymers based upon them. To give a more complete picture of the contemporary state of these fields of organophosphorus chemistry we also mention some of the most important and interesting investigations carried out outside the Kazan' school by Soviet and foreign scientists.

In 1903–05 A. E. Arbuzov, who was studying the structure of phosphorous acid and its organic derivatives, first isolated in a pure form the neutral esters of phosphorous acid and demonstrated the possibility of converting them into the corresponding esters of alkylphosphonic acids by the action of alkyl halides[1]. This remarkable reaction, which received the name of the Arbuzov rearrangement, subsequently became an important method of synthesising various esters of phosphonic acids and oxides of tertiary phosphines; it was studied in detail by A. E. Arbuzov and his students and by several other investigators. A. E. Arbuzov regarded the rearrangement of phosphite esters under the action of alkyl halides as a two-stage process. In the first stage an unstable product is formed, which then decomposes with the liberation of an alkyl halide and the ester of an alkylphosphonic acid:

$$(RO)_3P + R'X \rightarrow (RO)_3P\begin{matrix}R'\\X\end{matrix} \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}R' + RX.$$

It was shown later[2] that in addition to esters of phosphorous acid the esters of phenylphosphonous and diphenylphosphinous acids are capable of undergoing the reaction. The rate of isomerisation is considerably increased as alkoxyl groups in the phosphite ester are replaced by phenyl radicals. The rate of isomerisation of the phosphite esters falls in the order: $CH_3O > C_2H_5O > C_3H_7O >$ iso-C_4H_9O.

The Arbuzov rearrangement proceeds most readily with alkyl iodides and least well with alkyl chlorides.

The above studies, which were described in A. E. Arbuzov's Master's and Doctoral Theses formed the basis for a further extension of the investigations into the field of the rearrangement of esters of phosphorus(III) acids into phosphorus(V) compounds. One of the interesting and important problems is the effect of the structure of the phosphorus-containing components and of the alkyl halide on the rate and nature of the Arbuzov reactions that take place.

The success of B. A. Arbuzov and Rizpolozhenskii[3] and of Razumov[4] in synthesising esters of alkylphosphonous and dialkylphosphinous acids allowed their rearrangement into the corresponding esters of dialkylphosphinic acids and oxides of tertiary phosphines to be studied. The considerable increase in the rate of rearrangement on replacing an alkoxy-group by alkyl can be explained in terms of the positive inductive effect of alkyl groups[4].

A. E. Arbuzov was the first to describe the rearrangement of thioesters of phosphorus(III) acids, with the example of the thioesters of diphenylphosphinous acid:

$$PSR + R'Hal \longrightarrow P\begin{matrix}S\\R'\end{matrix} + RHal,$$

which is partly complicated by the formation of side-products[2,5,6]. With thiophosphites, substitution occurs instead of the Arbuzov rearrangement. The rearrangement of amido-esters of phosphorous acid [phosphoramidite esters] has been effected[7]:

$$RO\!\!>\!\!PNR'_2 + R''Hal \longrightarrow \left[RO\!\!>\!\!\overset{+}{P}\!\!<\!\!\begin{matrix}NR'_2\\R''\end{matrix}\right]Hal^- \longrightarrow RO\!\!>\!\!\overset{O}{P}\!\!<\!\!\begin{matrix}R''\\NR'_2\end{matrix} + RHal.$$

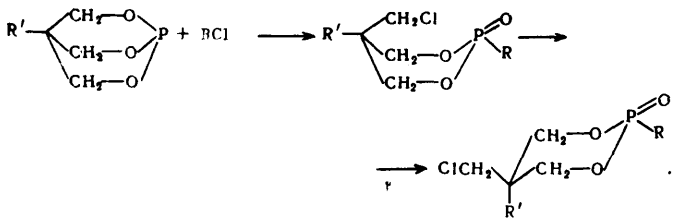
Interesting substances for studying the Arbuzov reaction were the cyclic esters of phosphorous acid, synthesised by A. E. Arbuzov, Rizpolozhenskii, Zoroastrova, and Razumova. The structure of the final products of the rearrangement depend on the size of the ring and the number and nature of the substituents in it[5,8]. Ethyleneglycol hydrogen phosphite and propylene glycol hydrogen phosphite, which contain five-membered rings, undergo the Arbuzov rearrangement with ring opening. The alicyclic product of the rearrangement can be cyclised by further heating:

$$R{-}CHO\!\!>\!\!POR' + R''Hal \rightarrow HalCH_2CHROP\begin{matrix}OR'\\\|O\\R''\end{matrix} \longrightarrow R{-}CHO\!\!>\!\!P\begin{matrix}R''\\\|O\end{matrix} + R'Hal.$$

Tetramethylethylene glycol hydrogen phosphite and methoxymethylethylene glycol hydrogen phosphite and esters with six-membered rings rearrange without rupture of the ring. These results have been confirmed by thermographic studies[9].

The rearrangement of hydrogen phosphite esters of pyrocatechol and of salicylic acid[10] and of spiro-diphosphites[11] under the action of alkyl halides takes place with retention of the cyclic structure. For bicyclic phosphites the Arbuzov reaction takes place with breaking of the ring

and replacement of the boat conformation by the energetically more stable chair conformation.



The Arbuzov rearrangement has been studied for diphosphites, esters of pyrophosphorous acid, and mixed anhydrides of phosphorous and carboxylic acids. In the last instance the reaction leads mainly to esters of ketophosphonic acids[12]:

$$(RO)_2POCOCH_3 + R'Hal \rightarrow (RO)_2P(O)R' + CH_3COHal$$

$$(RO)_2POCOCH_3 + CH_3COHal \rightarrow (RO)_2P(O)COCH_3 + CH_3COHal.$$

Kamai, Kuznetsov, and Valetdinov found that cyano-substituted esters of phosphorous acid do not undergo the Arbuzov rearrangement[13]. This is evidently because of the considerable negative inductive effect of the cyano-group, which lowers the electron density at the phosphorus(III) atom. Abramov and Khairullin[14] showed that the Arbuzov rearrangement proceeds normally for several mixed esters with one or two tertiary chloro-substituted radicals.

Study of the influence of the structure of the halogeno-derivatives on the course of the Arbuzov reaction showed that in addition to primary alkyl halides the rearrangement proceeds normally with primary arylalkyl halides, triarylmethyl halides, and acetylenic derivatives with a halogen atom at the triple bond[7]. As a result of the reaction of neutral esters of phosphorous acid with primary halides containing various heterocyclic radicals, B. A. Arbuzov and coworkers obtained esters of phosphorous acids with an α-oxide ring, thiazole, isoxazole, quinoxazole, furyl, phenthiazine, and various other radicals[15].

With secondary alkyl halides the rearrangement is more difficult and is often accompanied by the formation of alkenes. As Pudovik showed, the reaction of secondary halogenoallyl compounds and tertiary halogenoacetylenic compounds with phosphites is accompanied by allyl or acetylene–allyl rearrangement[16]:

$$R'CHHal{-}CH{=}CH_2 + (RO)_3P \rightarrow R'CH{=}CH{-}CH_2P(O)(OR)_2 + RHal$$

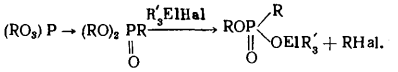
$$(CH_3)_2CCl{-}C{\equiv}CH + (RO)_3P \rightarrow (CH_3)_2C{=}C{=}CH{-}P(O)(OR)_2 + RCl.$$

When esters of phosphorous acid react with dihalogeno-derivatives with the halogens at primary carbon atoms either one or both halogen atoms react, depending on the conditions. With halogeno-derivatives having the halogens at secondary or tertiary carbon atoms as well as primary, molecules of hydrogen halide or halogen are lost and unsaturated compounds are formed[8].

In 1945 Kamai and Egorova observed that trialkyl phosphites readily undergo the Arbuzov rearrangement with carbon tetrachloride to form esters of trichloromethylphosphonic acid. Subsequently[17] this reaction was extended to a series of other alkyl esters of phosphorous, pyrophosphorous, and phosphinic acids.

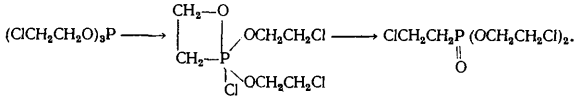
Derivatives of phosphonic acids are obtained by the Arbuzov rearrangement when various functional groups are present in the molecule of the halogen-containing compound. A. E. Arbuzov and Dunina obtained esters of phosphonocarboxylic acids by the reaction of phosphites and esters of α-halogenocarboxylic acids. With α-halogeno-substituted ethers and acetals, alkoxy- and dialkoxy-alkylphosphonates are formed; with acyl halides, the esters of ketophosphonic acids[8].

The Arbuzov rearrangement with alkylsilicon and alkyltin halides, first studied by B. A. Arbuzov, Pudovik, and Grechkin, proceeds anomalously and leads to the formation of compounds with a P–O–El bond. Malatesta[182] proposed a reaction mechanism including in the first stage the preliminary isomerisation of the phosphite esters into the corresponding esters of alkylphosphonic acids, which then react with the silicon and tin halides:



Later Pudovik and Muratova[18] confirmed and developed the Malatesta scheme, by showing that esters of phosphorus(III) acids are capable of forming unstable intermediate complexes with alkyltin and alkylsilicon halides; under mild conditions there is a rearrangement of these phosphite and phosphonite esters into phosphinate esters and tertiary phosphine oxides. These authors also studied in detail the reaction of alkylphosphonate esters with various halogen-containing compounds.

An anomalous course of the Arbuzov rearrangement was observed by B. A. Arbuzov and coworkers for α-bromonitrohydrocarbons, nitrosyl chloride, cyanogen chloride, dibenzoylbromomethane, tribenzoylbromomethane, and the halogeno-derivatives of some β-disulphones[15]. Phosphite esters with halogen atoms in the ester radicals at the α- or β-carbon atom were shown by Kabachnik and Rossiiskaya to undergo intramolecular isomerisation when heated or distilled[8]:



It was found subsequently that γ-, δ-, and ϵ-halogen-substituted phosphites isomerise in a similar manner. Pudovik and Faizullin synthesised a large number of β-chloro-substituted esters of phosphorus acids by the addition of acid chlorides of phosphorus(III) and phosphorus(V) acids to unsymmetrical α-oxides of alkenes[19]. It has been shown that all these reactions take place with participation of hydrogen chloride. The dependence of the order of breaking of the oxide ring on the structure of the original alkene oxide has been established. Nuretdinova[20] obtained a series of products of the addition of phosphorus(III) chloride and halogenophosphines to ethylene sulphide [thiairan] and propylene sulphide [1,2-epithiopropane].

The considerable experimental material which has accumulated in studying the Arbuzov rearrangement has allowed a more profound development of ideas on the mechanism of this interesting reaction. The two-stage scheme for the course of the reaction in the Arbuzov rearrangement, proposed by A. E. Arbuzov in 1905, was subsequently confirmed by him and by other investigators.

A. E. Arbuzov and Nesterov[21] obtained a whole series of new products of the addition of alkyl halides to triphenyl phosphite and studied their thermal decomposition. For a long time intermediate products of the rearrangement could not be isolated for aliphatic esters of phosphorus(III) acids. In 1954 Abramov and Karp[22] observed indirectly the formation of intermediate products in the reaction of trialkyl phosphites with various $\alpha\beta$-dihalogenoalkyl esters. Viscous non-crystalline substances were obtained, which on heating decomposed in accordance with the second stage of the Arbuzov reaction.

The formation of intermediate products was confirmed by the methods of physicochemical analysis[23] and by thermographic investigations[24], successfully applied by B. A. Arbuzov and coworkers to trialkyl phosphite–alkyl halide systems. For most of the reactions studied the thermograms had two exothermic effects, corresponding to the two stages of the rearrangement. Razumov and Bankovskaya[25] first succeeded in isolating in a pure state and studying the properties of the intermediate products of the Arbuzov rearrangement, which formed in the reaction of esters of diethylphosphinic acid with alkyl halides. The decomposition of the intermediate products takes place at room temperature or on slight heating:

$$(C_2H_5)_2POR + R'X \rightarrow (C_2H_5)_2\overset{R'}{\underset{X}{P}}{-}OR \rightarrow (C_2H_5)_2\overset{O}{\underset{R'}{P}} + RX.$$

On the basis of published data and the results of their own investigations, Razumov and Bankovskaya concluded that, depending on the nature of the phosphorus-containing components, the alkyl halide, and the solvent, the intermediate products can be a whole range of structures with various degrees of polarity—from ionic to covalent.

Important problems in studying the mechanism of the Arbuzov reaction are those concerning the nature of the first and second stages of the rearrangement and about the ratio of their rates. Kinetic investigations of the rearrangement, made by A. E. Arbusov and Nesterov[21], Zawidzki and Staronka[183], and Kosolapoff[184] showed that the process is complex. The reactions were usually carried out in the absence of a solvent, which brought about the appearance of an autocatalytic effect and complicated the interpretation of the results obtained[5]. Despite the absence of strict kinetic proofs the nature of the first stage of the Arbuzov rearrangement—the addition of alkyl halides to the esters of the phosphorus(III) acids—is not in dispute. Most authors regard it as a second-order S_N2 reaction. There are various views about the nature of the second stage of the rearrangement—the decomposition of the intermediate addition product. Gerrard and Green[185] consider it as an S_N2 reaction, on the basis of stereochemical investigations. Later the stereospecific S_N2 mechanism of the second stage of the rearrangement was supported and investigated by Berlin and coworkers[26]. Pudovik, in studying the rearrangement of phosphite esters containing unsymmetrical allyl radicals, concluded that the second stage of the rearrangement of trialkyl phosphites with primary saturated or unsaturated radicals is brought about on the basis of an S_N2 mechanism. With phosphites which contain secondary radicals the reaction proceeds by a mixed mechanism predominantly of the S_N1 type[27]. On the basis of a study of the kinetics of the decomposition of the addition products of alkyl halides to esters of diethylphosphinous acid, Razumov and Bankovskaya consider that the second stage of the Arbuzov reaction is a first-order unimolecular reaction[25]:

$$(C_2H_5)_2\overset{R'}{\underset{OR}{P}} \xrightarrow{\text{slow}} (C_2H_5)_2\overset{R'}{\underset{O}{P}} + R^+$$

$$R^+ + X^- \xrightarrow{\text{fast}} RX$$

Buck and Yoke[28] came to analogous conclusions in a conductimetric study of the reaction of tributyl phosphite with ethyl iodide in acetonitrile. Nesterov[29] later made some interesting investigations of the reactivity of quasi-phosphonium compounds.

Opinion is also divided over the relation between the rates of the first and second stages of the Arbuzov rearrangement. Buck and Yoke, and Razumov and Bankovskaya consider the second stage of the rearrangement to be the slower stage, which determines the rate of the overall reaction. According to the results of the Aksnes[30], who made a kinetic study of the reaction of ethyl iodide with several phosphites, phosphonites, and phosphinites [and triphenylphosphines] by quantitative infrared spectroscopy, the ethyl iodide concentration remains almost constant throughout the rearrangement. This suggests the absence of a significant accumulation of intermediate product indicating that the first stage of the Arbuzov rearrangement is rate-determining. Fainshtein and Gonikberg, who studied the reaction of triethyl phosphite with ethyl iodide at high pressures, also did not observe the accumulation of an intermediate product during the rearrangement[31].

The above mechanism of the Arbuzov rearrangement is evidently not the only one possible for all types of reaction[32]. As is well known, Rumpf earlier proposed an ion-chain mechanism for the Arbuzov rearrangement. To explain the reaction of phosphorus(III) esters with carbon tetrachloride, Kamai and Kharrasova introduced a radical-chain mechanism, which was subsequently confirmed experimentally by these authors and various other investigators[17]:

$$CCl_4 + h\nu \rightarrow \dot{C}Cl_3 + Cl^\cdot,$$

$$(RO)_3P + \dot{C}Cl_3 \rightarrow (RO)_3\dot{P}CCl_3 \xrightarrow{CCl_4} (RO)_3\overset{+}{P}CCl_3\overline{Cl} + \dot{C}Cl_3$$

$$\downarrow$$

$$(RO)_2PCCl_3 + RCl$$

$$\parallel$$

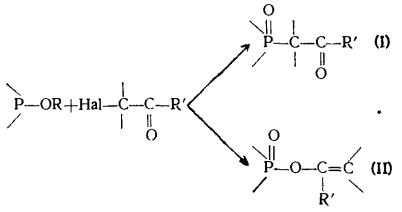
$$O$$

Recently Cadogan and Sharp[33] found that in the absence of ultraviolet radiation or radical initiators the reaction of triethylphosphite with carbon tetrachloride is apparently heterolytic.

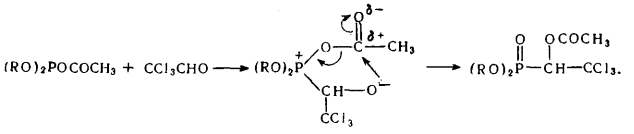
In concluding the discussion of the mechanism of the Arbuzov rearrangement it should be noted that despite the considerable number of investigations that have been made, its mechanism is still not fully explained: further kinetic and stereochemical investigations are needed to obtain a more complete picture of the course of this interesting reaction.

In recent years there has been great interest in studying the reactions of trialkyl phosphites with α-halogeno-carbonyl compounds. It was suggested initially that all reactions of this type proceed according to the scheme of the Arbuzov rearrangement with the formation of esters of keto- and aldehydo-phosphonic acids[32]. It was subsequently shown that although in several instances these products are actually formed to a certain extent, most of

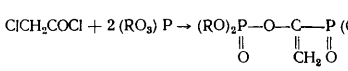
the reactions of trialkyl phosphites with α-halogenocarbonyl compounds proceed "anomalously" with the formation of unsaturated esters of phosphoric acid. Perkow[188] first stated the "anomalous" course of the reaction for α-halogenoaldehydes: it was proposed for α-halogenoketones somewhat later by one of us in Kazan'[34] and by the American chemists Allen and Johnson[187]:



Esters of phosphorus(III) acids react with α-halogenoaldehydes, usually with the formation of unsaturated esters of phosphoric acid (II). However, the reaction of mixed anhydrides of dialkyl phosphites and acetic acid with chloral proceeds without liberation of alkyl halide, with the formation of the acetates of the dialkyl esters of 2,2,2-trichloro-α-hydroxyethylphosphonic acids[35]:



With α-halogenoketones the formation of (I), (II), or mixtures of the two products depends on the structure of the α-halogenoketone, the number and nature of the halogen atoms, the reaction temperature, and the solvent. Pudovik has shown[36] that in the reactions of trialkyl phosphites with chloro-, bromo-, and iodo-acetones, and ω-chloro-, ω-bromo-, and ω-iodo-acetophenones, a mixture of (I) and (II) is formed, the relative amount of (II) rising in the series I < Br < Cl, and decreasing with increase in the reaction temperature. Going from primary to secondary α-halogenoketones leads to a relative increase in the concentration of unsaturated esters of phosphoric acid in the reaction products. As B. A. Arbuzov and coworkers showed[37], α-halogenoketones with the halogen atom at a tertiary carbon atom react with trialkyl phosphites exclusively with the formation of (II). The reaction of trialkyl phosphites with cyclic α-halogeno-ketones[36,38], with di- and tri-halogenocarbonyl compounds containing halogen atoms in the α position to the carbonyl group, with 2-halogeno-1,3-diketones, with α-chlorophosphonoacetone[36], and with esters of α-halogeno-β-keto-acids[34,36] also proceed analogously. Evidently the presence of electronegative groups at a carbon atom connected with a halogen causes a stronger polarisation of the molecule of the α-halogenocarbonyl compound and facilitates the formation of an unsaturated phosphate[32]. The reaction of α-halogenocarbonyl compounds with phosphonite esters usually proceeds in the same direction as with trialkyl phosphites[36,39,40]. As regards the acid chlorides of α-halogenocarboxylic acids, several authors have shown that both halogen atoms are involved in the reaction with a trialkyl phosphite[34]:

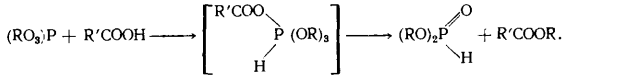


Reactions with α-halogenocarbonyl compounds have now been studied for an extremely wide circle of ester-amides of phosphorus(III) acids. As Abramov and Il'ina showed[41], the reaction of α-halogenoaldehydes and α-halogenoketones with the monoamides and diamides of phosphorous acid takes place preferentially with the formation of unsaturated esters of phosphoramidic and phosphorodiamidic acids.

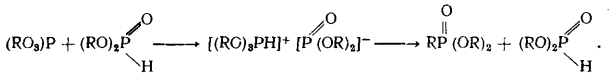
Several other scientists were concerned with studying the Perkov reaction and extending its field of use. A considerable number of investigations have been devoted to finding the mechanism of this interesting reaction. Theories have been developed about initial attack by the nucleophilic phosphorus atom of the trialkyl phosphite at the oxygen or carbon atom of the carbonyl group, halogen atom, or α-carbon atom[34].

The numerous investigations of the Kazan' school of organophosphorus chemists and of a whole series of other Soviet and foreign scientists have shown that the esters of the phosphorus(III) acids readily react not only with organic halogen derivatives, but also with a wide circle of electrophilic reagents which do not contain a halogen atom. Reactions of this type are quite diverse and of great theoretical interest. In most instances they are considered as proceeding according to the Arbuzov rearrangement scheme[32].

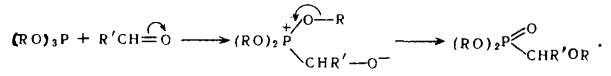
In 1951, A. E. Arbuzov and Alimov studied the reaction of some inorganic acids with trialkyl phosphites, leading to the formation of dialkyl hydrogen phosphites. Trialkyl phosphites react analogously with certain organic acids and their anhydrides[32]:



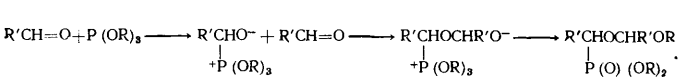
As Pudovik and Rakov showed recently[42], the reaction of trialkyl phosphites with acid esters of phosphorous and phosphonous acids leads to the formation of esters of phosphonic acids:



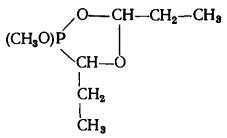
The reactions of α-ester-amides with triethyl phosphite leads, according to the results of Ivanov and coworkers, to the formation of esters of dialkylaminomethylphosphonic acids (in the presence of acetic or hydrochloric acids) or esters of alkoxymethylphosphonic acids (in the presence of ethyl iodide)[43]. Quite an interesting reaction is that of phosphites with carbonyl compounds. In 1954, when heating trialkyl phosphites with aldehydes Abramov isolated esters of α-alkoxyalkylphosphonic acids. The following scheme was proposed for this reaction[32]:



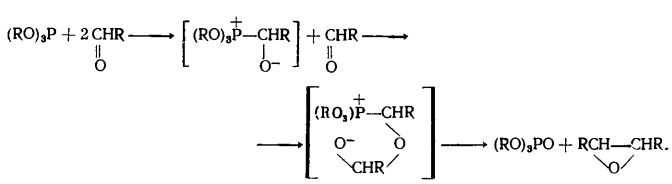
Alimov obtained similar results in studying the reaction of aldehydes with tetraethyl pyrophosphite and a diethyl acyl phosphite. Later Yakubovich and Ginsburg showed[44] that only aromatic aldehydes react with alkyl phosphites according to the Abramov scheme. Saturated aliphatic aldehydes form products of the addition of two molecules of aldehyde to one molecule of phosphite.



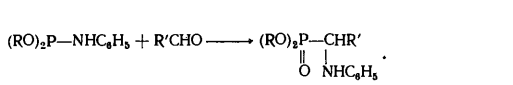
As Ramirez has shown[45], prolonged reaction of three moles of propionaldehyde with one mole of trimethyl phosphite at room temperature leads to a cyclic tetra-alkoxy-alkylphosphorane [sic; the compound shown is 2,5-dimethyl-4-methoxy-1,3,5-dioxaphospholan (Ed. of Translation)]:



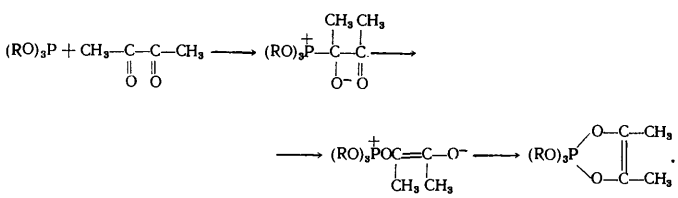
On heating trialkyl phosphites with furfural and benaldehyde B. A. Arbuzov and Zoroastrova observed the oxidation of phosphites to phosphates and the formation of difurylethylene oxide and stilbene oxide respectively[7]:



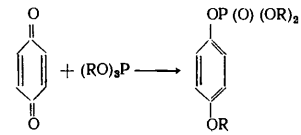
The alkene oxide which is formed in converted further by a second trialkyl phosphite molecule into the alkene. The reaction with triamidophosphites proceeds similarly[5]. Abramov and Il'ina assumed in studying the reactions of a series of *N*-phenylphosphoroamidites with aldehydes and ketones that they proceed by a scheme similar to that for trialkyl phosphites[41]. More detailed study of the structure of products formed in these and analogous reactions by Evdakov and coworkers[46], by Pudovik, and by Hudson and coworkers[47], showed that they are aminophosphinic esters [esters of aminoalkylphosphonic acids]:



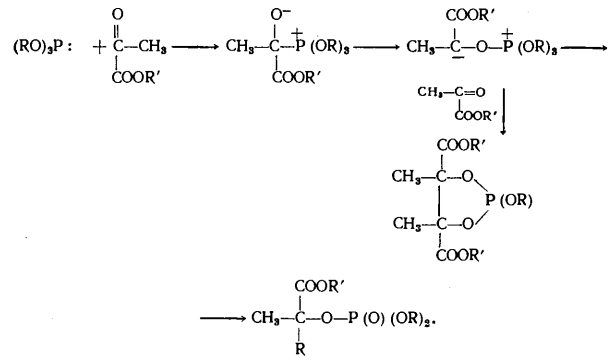
Ramirez and coworkers[45], Kukhtin and Kirillova[48,49], and Birum and Dever[188] studied the reaction of trialkyl phosphites with α-diketones. It was found[48,49] that the reaction of phosphites and phosphoroamidites with biacetyl at room temperature gives stable 1 : 1 addition compounds—the cyclic 1,3,2-dioxaphospholes:



By carrying out the reaction at a higher temperature, Kukhtin and coworkers isolated—in addition to the 1,3,2-dioxaphospholes—products which they regarded as α-alkoxy-β-keto-phosphonates. The reaction of trialkyl phosphites with 1,2-cyclohexadione proceeds in two directions, as for biacetyl[50]. In the reaction of phosphites with methylphenylglyoxal and *o*-quinones, Kukhtin and Kirillov obtained, irrespective of the reaction conditions, compounds with a 1,3,2-dioxaphosphole structure[51,52]. The addition of trialkyl phosphites to *p*-quinones takes place in the 1,6-position and leads to the formation of the corresponding phosphates[45]:

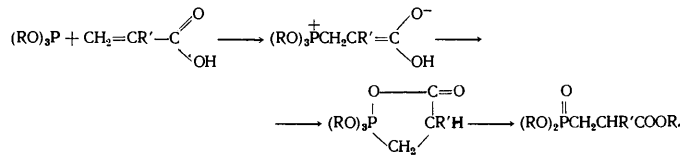


The reaction of esters of α-ketocarboxylic acids with trialkyl phosphites was studied by Pudovik and Konovalova and by Ramirez and coworkers. It was found[45,53] that under mild conditions (0–10°C) the phosphites react with two molecules of pyruvic ester to form the corresponding 1,3,2-dioxaphospholanes. At a higher temperature (80–100°C) in addition to the latter, dialkyl-α-alkyl-α-alkoxycarbonylethyl phosphates are formed, as Pudovik and Konovalova showed. They proposed the following reaction scheme:

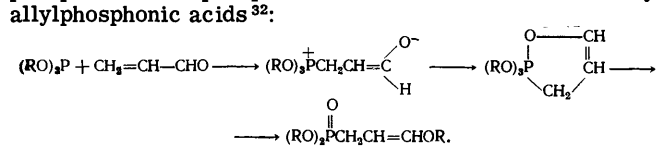


In the reaction of trialkyl phosphites with ethyl mesoxalate only the corresponding dialkyl-$\alpha\alpha$-di(ethoxycarbonyl)-alkyl phosphates were isolated, irrespective of the reaction conditions[54].

Kamai and Kukhtin investigated the reactions of esters of phosphorus(III) acids with $\alpha\beta$-unsaturated acids and aldehydes. It was shown[32] that trialkyl phosphites are readily added to $\alpha\beta$-unsaturated acids to form the esters of β-phosphonocarboxylic acids:

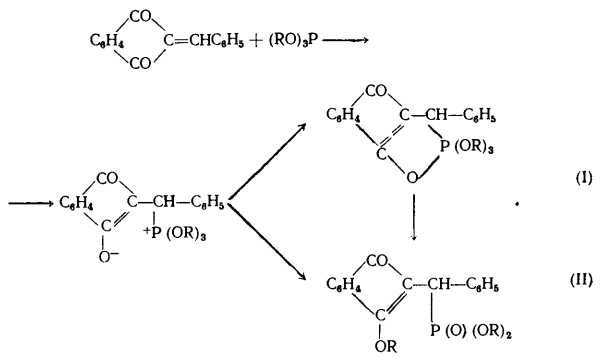


The intermediate cyclic products could not be isolated although several experimental facts show that they are formed. The reaction of trialkyl phosphites with alkynylcarboxylic acids leads to esters of β-phosphonocarboxylic acids[55]. With $\alpha\beta$-unsaturated aldehydes neutral esters of phosphorous and phosphonous acids form esters of alkoxyallylphosphonic acids[32]:



According to Ramirez' results, the reaction of $\alpha\beta$-unsaturated ketones is considerably affected by the structure of the original ketone and by the conditions[56]. B. A. Arbuzov and coworkers showed that the reaction of benzylideneindandione with trialkyl phosphites leads to the formation of either cyclic unsaturated phosphoranes [1,2-oxaphospholes (Ed. of Translation)] (I) or esters of the enolic

forms of indan-1,3-dion-2-ylbenzylphosphonic acids (II), depending on the temperature[57]:

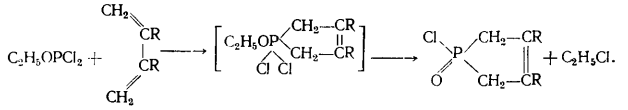


(I)

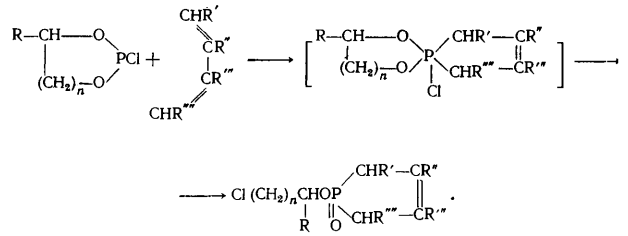
(II)

The reactions of acid chlorides of phosphorus(III) acids with diene hydrocarbons, $\alpha\beta$-unsaturated aldehydes, ketones, and acids, which have been widely studied in recent years, can also be considered as a variety of the Arbuzov rearrangement.

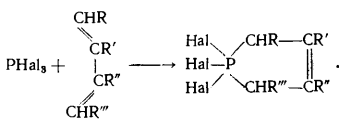
In 1953 a patent of McCormack reported the production of phosphorus-containing heterocyclic compounds in the reaction of diene hydrocarbons with aryl- and alkyl-dichlorophosphines. With the acid chlorides of esters of phosphorous acid, the 1,4-addition is accompanied by a simultaneous Arbuzov rearrangement, as B. A. Arbuzov and Shapshinskaya showed[7]:



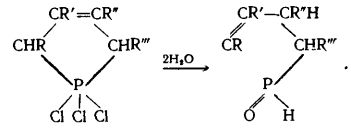
Similar reactions of this type were studied by B. A. Arbuzov and Shapshinskaya and by Petrov and Razumova using the acid chlorides of alkylene glycol esters of phosphorous acid and various diene hydrocarbons[58,59]. The reaction products are always five-membered heterocyclic compounds—derivatives of 1-oxa-1-phospha-3-cyclopentene:



B. A. Arbuzov and Vizel'[60] and Korte and coworkers[61] independently showed that trihalogeno-compounds of phosphorus are capable of adding to diene hydrocarbons to form derivatives of 1,1,1-trihalogeno-1-phosphacyclopent-3-ene. They were first isolated in a pure form by B. A. Arbuzov and Vizel':

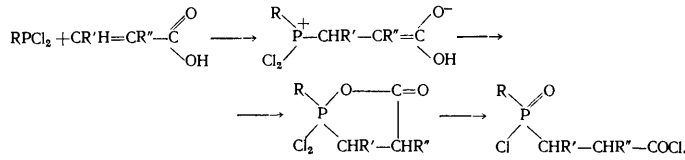


The reactions of derivatives of 1,1,1-trichloro-1-phosphacyclopent-3-ene are usually accompanied by migration of the double bond in the ring from the 3, 4 to the 2, 3 position:



1,1,1-tribromophosphacyclopent-3-enes have no tendency for migration of the double bond. Such unusual behaviour of the trihalogenophosphacyclopentenes allowed a large number of phosphacyclopentene derivatives with various locations of the double bond in the ring to be synthesised[62].

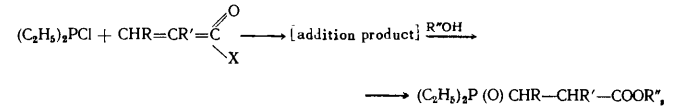
As Khairullin and Pudovik and their coworkers showed, the reaction of alkyl- and aryl-dichlorophosphines with $\alpha\beta$-unsaturated acids leads to the formation of the acid chlorides of alkyl- and aryl-(β-chloroformyl)alkylphosphinic acids[63]:



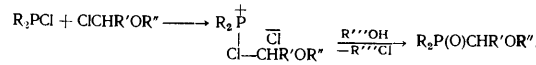
Nitriles of dialkylphosphinylcarboxylic acids were obtained by an analogous reaction with the amides of unsaturated acids:

$$R_2PCl + CH_2{=}CHCONH_2 \rightarrow R_2P(O)CH_2CH_2CN + HCl.$$

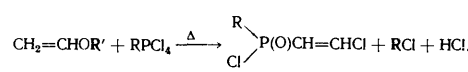
Kamai and Tsivunin studied the condensation of chlorodiethylphosphine with $\alpha\beta$-unsaturated acids and their acid chlorides. When the resulting addition products were treated with alcohol, esters of diethylphosphinylcarboxylic acids were obtained[64]:



where X = Cl or OH. The same authors investigated the reaction of secondary chlorophosphines with various halogen-containing organic compounds: α-halogeno-substituted ethers and sulphides, certain mono- and di-halogeno-derivatives of hydrocarbons, and α-halogenoaldehydes. The corresponding addition products are always formed: when these are decomposed with water, alcohols, or hydrogen sulphide, the oxides or sulphides of tertiary phosphines are liberated[65]:

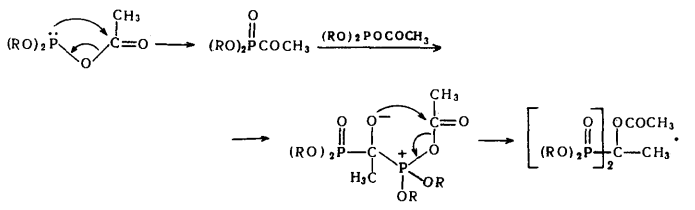


The reaction of various phosphorus(V) halides with vinyl ethers was also studied[66,67]. The thermal decomposition of the complexes of ethyl- and phenyl-tetrachlorophosphorus with vinyl ethers gave ethyl- or phenyl-β-chlorovinylphosphinic chloride:



To conclude the review of the investigations of the Kazan' school of organophosphorus chemists in the field of conversions of phosphorus(III) derivatives into phosphorus(V) compounds we will discuss the thermal rearrangements of unsaturated esters of phosphorous and phosphonous acids. Pudovik and Rakov showed[42] that neutral esters of phosphorous acid with saturated lower

radicals are rather stable on heating, contrary to the results of Simon and Schulze[189]. Mixed anhydrides of phosphorous and acetic acid isomerise at elevated temperatures into ketophosphonate esters, which are subsequently converted into the acetates of methylbis(dialkyl phosphono)-carbinols[68]:



As A. E. Arbuzov and Nikonorov first showed[69], allyl and benzyl diphenylphosphinates readily undergo thermal rearrangement, with the formation of the corresponding phosphine oxides. Later the authors of the present review found that the rate of thermal isomerisation increases considerably on going from the allyl esters of phosphorous acid to the esters of phosphonous and especially phosphinous acids. When the allyl radical has a substituent at the α and γ carbon atoms, the rearrangement is accompanied by inversion of the unsaturated radical[70,71]:

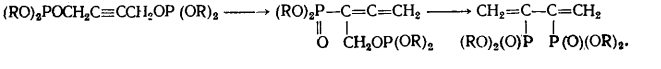
$$R_2POCHR'CH{=}CHR'' \xrightarrow{\Delta} R_2P(O)CHR''CH{=}CHR'.$$

The thermal isomerisation of the prop-2-ynyl esters of phosphorus(III) acids takes place especially readily at temperatures close to room temperature[70]. The products are esters of allenylphosphinic acids or allenylphosphine oxides, in many instances capable of undergoing a further prototropic conversion into prop-1-ynyl phosphonates and prop-1-ynylphosphine oxides, that is, an acetylene–allene–acetylene rearrangement takes place:

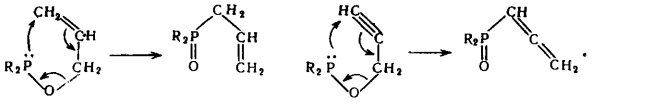
$$R_2POCH_2C{\equiv}CH \rightarrow R_2P(O)CH{=}C{=}CH_2 \rightarrow R_2P(O)C{\equiv}C{-}CH_3.$$

The American scientists Boisselle and Meinhardt[190] and Mark[191] observed the acetylene–allene rearrangement of esters of phosphorus(III) acids simultaneously with the authors of the present review, but isolated only esters of allenylphosphinic acids and allenylphosphine oxides.

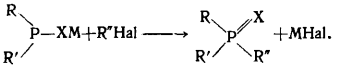
Pudovik and Aladzheva carried out the acetylene–allene–diene rearrangement of tetra-alkylbutyn-1,4-diol diphosphites and obtained 2,3-bis(dialkylphosphono)buta-1,3-dienes[70,72]:



On the basis of the above investigations the authors concluded that the thermal isomerisations of $\beta\gamma$-unsaturated esters of phosphorus(III) acids are intramolecular S_Ni rearrangements, proceeding through a five-centre cyclic transition state:



In addition to the Arbuzov rearrangement, the most important method of preparing organophosphorus compounds is the Mikhaelis–Bekker reaction—the reaction of salts of phosphorous or phosphinous acids and their thioanalogues with various halogen derivatives:



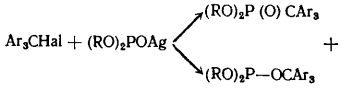
A large number of esters of phosphinic and thiophosphinic acids and their derivatives have been synthesised by this method[73]. Several studies in this direction were completed by the Kazan' organophosphorus chemists, but in their investigations they paid much attention to studying reactions which departed from the usual Mikhaelis–Bekker scheme. These investigations led to the discovery of new, interesting, and important reactions.

In 1929 A. E. and B. A. Arbuzov found[74] that in the reaction of sodium diethyl phosphite with bromotriphenylmethane the product is not diethyl triphenylmethylphosphonate (as for chlorotriphenylmethane) but the triphenyl free radical:

$$(C_2H_5O)_2PONa + (C_6H_5)_3CCl \rightarrow (C_6H_5)_3CP(O)(OC_2H_5)_2 + NaCl$$

$$2(C_2H_5O)_2PONa + 2(C_6H_5)_3CBr \rightarrow 2(C_6H_5)_3C^{\cdot} + [(C_2H_5O)_2PO]_2 + 2NaBr.$$

This investigation led to the discovery of a new, quite simple, and elegant method of obtaining free radicals of the triarylmethyl series. A. E. Arbuzov and Valitova later showed what happens to the phosphorus-containing part of the reaction: ethyl hypophosphate was identified in the products[75]. Electron paramagnetic resonance was used recently to confirm the formation of free radicals in this reaction[76]. Free radicals were also obtained in the reaction of sodium diethyl phosphite with certain other triarylbromomethanes and in the reaction of lithium, potassium, rubidium, and caesium diethyl phosphites with bromotriphenylmethane[77]. The silver dialkyl phosphites are an exception; they react with the triarylhalogenomethanes to form triarylmethylphosphonates or mixed esters of phosphorous acid:

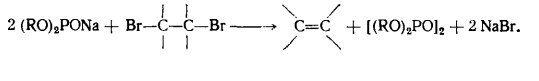


The halogenodiphenylmethanes react like the triarylhalogenomethanes with sodium diethyl phosphite[78]. Tetraphenylethane was isolated in the reaction of sodium diethyl phosphite with bromodiphenylmethane.

According to Pudovik and Tarasova, the reaction of triarylhalogenomethanes with the salts of ethylphosphonic acid or dialkyl hydrogen thiophosphites are much more complex than those with the salts of dialkyl hydrogen phosphites[79].

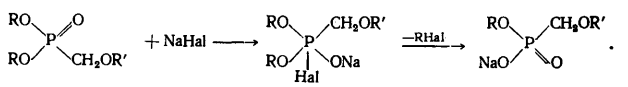
B. A. Arbuzov and Bogonostseva showed that in the reaction of sodium diethyl phosphite with dibenzoyl- and tribenzoyl-bromomethane, dibromobis(ethylsulphonyl)- and dichlorobis(ethylsulphonyl)-methane, the halogen derivatives are reduced to dibenzoyl- and tribenzoyl-methane and di(ethylsulphonyl)methane[80].

The reactions of salts of dialkyl hydrogen phosphites with 1,2-dihalogen derivatives—dibromostyrene, $\alpha\beta$-dibromopropionitrile, 9,10-dibromophenanthrene, tetramethylethylene dibromide, 1,2-dibromomethane, 1,2-dibromocyclohexane, and various other compounds[73,78,81]—proceeds by a similar scheme, with the formation of unsaturated compounds:

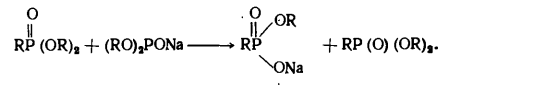


The reaction of salts of dialkyl hydrogen phosphites with α-halogeno-substituted ethers leads to esters of alkoxymethylphosphonic acids, according to the results of Abramov and coworkers[82]. It is interesting that in the distillation of the reaction mixture without separation of

the precipitate of metal halide, ester-salts (not distilling) of an alkoxymethylphosphonic acid are obtained:

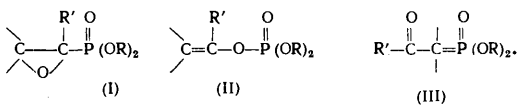


Petrov and coworkers explain the behaviour of ester-salts in these reactions by the alkylation of sodium dialkyl phosphite, formed in the first stage by the alkylphosphonates[83]:

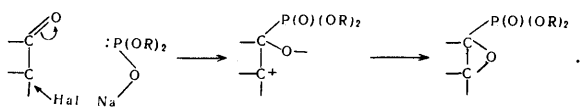


Pudovik and Tarasova showed recently that the formation of ester-salts is possible as the result of the isomerisation of sodium dialkyl phosphite in inert solvents at a temperature above 100°C.[84]

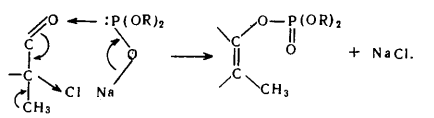
According to the results of B. A. Arbuzov and coworkers, reactions of sodium diethyl phosphite with α-halogenoketones takes place in a complex manner and, depending on the nature of the halogen, the reaction conditions, and the presence of substituents in the α-halogenoketone, lead to the formation of esters of epoxyphosphonic acids(I), unsaturated esters of phosphoric acid (II), or esters of β-ketophosphonic acids (III)[37,38,85]:



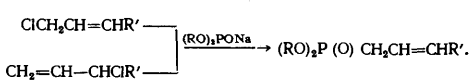
To explain the formation of (I), B. A. Arbuzov proposed a scheme including the initial addition of sodium diethyl phosphite at the carbonyl bond, with subsequent stabilisation of the bipolar ion formed:



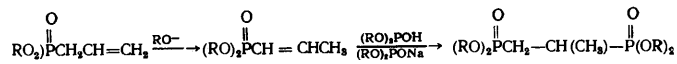
(II) is formed by addition to the oxygen atom of the carboxyl group:



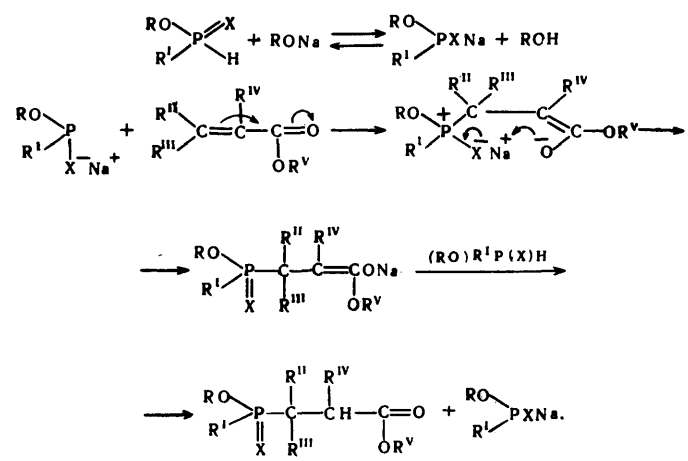
Interesting results were obtained by Pudovik in 1947 in studying the reactions of salts of dialkyl hydrogen phosphites and of thiophosphorous acids with α-halogenoallyl compounds[86,87]. In the reaction of sodium diethyl phosphite with allyl bromide, isomeric chlorobutenes, and chloro(methoxy)pentenes, esters of allyl- and substituted allyl-phosphonic acids were obtained. The reaction of secondary halogeno allyl compounds proceeds with an allyl rearrangement:



Subsequently, addition of sodium dialkyl phosphite takes place at the double bond of the unsaturated phosphonate esters formed in the first stage of the reaction and bis-(dialkyl phosphono)-derivatives are obtained:

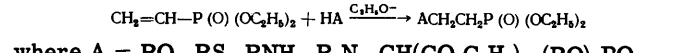


The results obtained form a basis for a new method of synthesis of esters of phosphonic [and phosphinic] and thiophosphinic [and thiophosphonic] acids developed by Pudovik and consisting in the addition of acid esters of phosphorous, thiophosphorous, and phosphonous [and phosphinous] acids to unsaturated compounds of the electrophilic type. A large number of esters of phosphonocarboxylic, phosphonodicarboxylic, bisphosphonocarboxylic, and phosphonoketocarboxylic acids was obtained as a result of the addition of unsaturated esters of phosphorus acids to esters of monobasic and dibasic unsaturated carboxylic acids of the ethylene and acetylene series and to esters of unsaturated keto-acids[87-89]:



Acid esters of phosphorus acids react similarly with nitriles and amides of unsaturated acids[87,89]. The additions to αβ-unsaturated ketones usually take place at the carbon–carbon double bond with the formation of esters of ketophosphonic and ketothiophosphonic [and ketophosphonic and ketothiophosphinic] acids[87,89,90]. With acetylenic ketones the addition takes place primarily at the carbonyl group with formation of esters of acetylenic α-hydroxyphosphonic [and α-hydroxyphosphinic] acids[91]. Exceptionally, acid esters of phosphorus acids are added at the carbonyl group of unsaturated aldehydes containing ethylenic and acetylenic bonds[87,91]. With α-unsaturated nitro-compounds and sulphones the addition occurs at the carbon–carbon double bond[92].

Pudovik found an important method of synthesising various derivatives of phosphonic and thiophosphonic acids—the addition of nucleophilic reagents to esters of unsaturated phosphonic acids. The simplest reaction of this type is "phosphonoethylation"—the addition of nucleophilic reagents to diethyl vinylphosphonate[87,93]:



where A = RO, RS, RNH, R_2N, $CH(CO_2C_2H_5)$, $(RO)_2PO$, $(RO)_2PS$, (RO)R'PO, etc. Pudovik and coworkers studied the addition of nucleophilic reagents to certain derivatives of vinylphosphonic esters: the esters of α- and β-cyano-vinylphosphonic acids[94], α- and β-alkoxycarbonylvinylphosphonic acids[88]. With the esters of β-alkoxycarbonyl- and β-cyano-vinylphosphonic acids the more electronegative

alkoxycarbonyl and nitrile groups determine the direction of the addition. Nucleophilic reagents add to esters of butadienylphosphonic and butadienylthiophosphonic acids in the 1,4 position[95]:

$$CH_2{=}CR{-}CH{=}CH{-}P(X)(OC_2H_5)_2 + AH \xrightarrow{RONa} ACH_2CR{=}CH{-}CH_2P(X)(OC_2H_5)_2$$

but to 2,3-bis(diethylphosphono)buta-1,3-diene in the 1,2 position[96]. In the esters of $\gamma\gamma$-dimethylallenylphosphonic acid the double bond in the $\alpha\beta$ position to the phosphono-group is the more active in nucleophilic addition[97]:

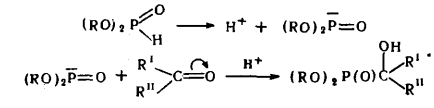
$$(CH_3)_2C{=}C{=}CH{-}P(O)(OR)_2 + HA \xrightarrow{RONa} (CH_3)_2C{=}CA{-}CH_2P(O)(OR)_2.$$

Depending on the ratio of the reactants in the reaction mixture, one or two molecules of nucleophilic reagent are added to esters of $\alpha\beta$-propynylphosphonic acid[98].

The addition of acid esters of phosphorus acids to unsaturated hydrocarbons of the ethylene and acetylene series, vinyl ethers, and halogenoalkenes does not take place under ionic catalysis conditions, according to Pudovik and Konovalova's results, but can be effected by a radical mechanism in the presence of peroxide compounds or by irradiating the reaction mixture with ultraviolet light[99]. Anti-Markovnikov addition occurs.

The addition of phosphorus-containing compounds with a labile hydrogen atom to a carbonyl group was first observed "by Marie and by Ville" with phosphorous and hypophosphorous acids[100]. A. E. Arbuzov and Azanovskaya put forward a scheme to explain the reaction of sodium diethyl phosphite with acetyl chloride; it was suggested that addition of the sodium salt at the carbonyl group initially gives an acetophosphonic ester[101].

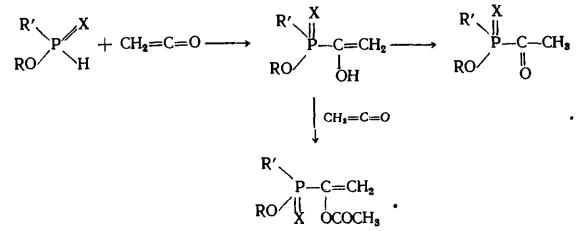
In 1950 Abramov proposed and subsequently developed extensively a method for the synthesis of esters of α-hydroxyalkylphosphonic acids, consisting in the addition of dialkylphosphoric acids and other acid esters of phosphorus acids to aldehydes and ketones[102]. The reactions of dialkyl phosphonates with aldehydes and ketones proceed with almost quantitative yields, usually in the absence of catalysts and solvents on holding the reaction mixtures at room or elevated temperatures[103]:



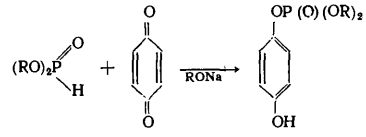
The possibility that the enol form of the dialkyl hydrogen phosphite takes part in the reactions is not ruled out[104].

Kabachnik and Tsvetkov[105] suggest the possibility of a termolecular reaction in the condensation of dialkyl hydrogen phosphites with aldehydes. In several instances the reactions are accelerated in the presence of alkali metal alkoxides which facilitate the formation of the dialkylphosphonium anion. Abramov and coworkers studied the addition of dialkyl hydrogen phosphites, dialkyl hydrogen thiophosphites, and acid esters of alkyl- and aryl-phosphonic acids to a large number of aldehydes and ketones of the aliphatic, aromatic, and heterocyclic series[103,104]. It was shown that the addition of acid esters of phosphorus acids is greatly facilitated with α-halogenocarbonyl compounds and certain other derivatives of aldehydes and ketones containing electro negative groups. The reactions with di-, tri-, and poly-chloro-substituted carbonyl compounds are particularly vigorous. Chloro-substituted dialkyl hydrogen phosphites, dialkyl hydrogen thiophosphites, and acid esters of phenylphosphonic acid add to aldehydes and ketones comparatively readily[106].

As Pudovik and Nikitina showed, acid esters of phosphorus acids react with ketens in the presence of pyridine or sulphuric acid, forming products by addition at the carbonyl group; under the conditions of the reaction the latter are partly or completely acetylated by a second molecule of the keten[107]:



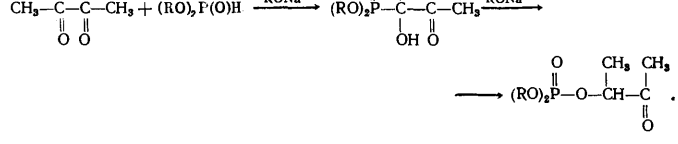
Mixed esters of dialkyl hydrogen phosphites and hydroquinone were obtained by the addition of dialkyl hydrogen phosphites to *p*-quinone in the presence of alkali metal alkoxides[108,109].



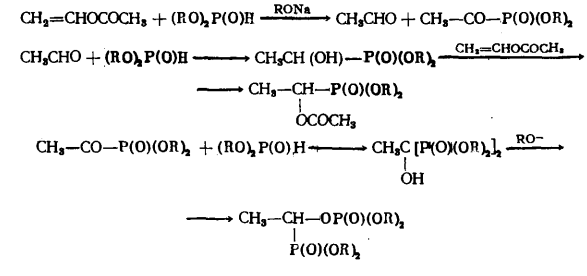
Rizpolozhenskii observed intramolecular addition at the carbonyl group in the reaction of alkyl dichlorophosphites [sic. presumably alkyl phosphorodichloridites] with diacetone alcohol in the presence of a base[110].

Interesting results were obtained in studying the reaction of the acid esters of phosphorus acids with carbonyl compounds containing electron-acceptor substituents in the α position to the carbonyl group. The addition here is accompanied by the rearrangement of the α-hydroxyalkylphosphonic esters formed initially into esters of phosphoric acid. Rearrangement was observed for esters of α-hydroxyalkylphosphonic acids with trichloromethyl[111] and cyano-[112] groups at the α-carbon atom.

Kukhtin and coworkers showed[113] that the reaction of dialkyl hydrogen phosphates with biacetyl at $> 100°C$ or on heating the reagents with sodium alkoxides also leads to esters of phosphoric acid:



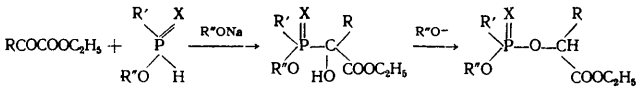
The phosphonate–phosphate rearrangement of bis(dialkylphosphono)carbinols was first observed by Pudovik and Konovalova in studying the reaction of dialkyl hydrogen phosphites with vinyl acetate[70]. The first stage of the reaction was the acetylation of the dialkyl hydrogen phosphite:



A special investigation of the reaction of acetophosphinic esters with dialkyl hydrogen phosphites showed that diphosphonocarbinols can be obtained only when the reaction is performed under mild conditions in the presence of diethylamine and at a temperature not exceeding 40–50°C. In the presence of alkaline catalysts they are rearranged into the esters of phosphoric acid. Somewhat later American scientists also observed the phosphonate–phosphate rearrangement[114]. The discovery of the phosphonate–phosphate rearrangement of diphosphonocarbinols enabled the mechanism of a series of other interesting reactions to be established[70]. For example, it was shown that the final products of the reaction of acetyl chloride and acetic anhydride with sodium diethyl phosphite are esters of phosphoric acid and not acetates of phosphonocarbinols, as had been suggested earlier:

$$CH_3COCl + (RO)_2PONa \rightarrow CH_3COP(O)(OR)_2 \xrightarrow{(RO)_2PONa} CH_3-C[P(O)(OR)_2]_2 \longrightarrow$$
$$\xrightarrow[(RO)_2P(O)H]{(RO)_2PONa} CH_3-CH(P(O)(OR)_2)-O-P(O)(OR)_2.$$

The mechanism of reaction of alcohols with esters of acetoxyvinylphosphinic acid has been demonstrated. A phosphonate–phosphate rearrangement was also observed in the reaction of acid esters of phoshorus acids with pyruvic[70] and mesoxalic[115] esters:



where R = CH_3, $CO_2C_2H_5$.

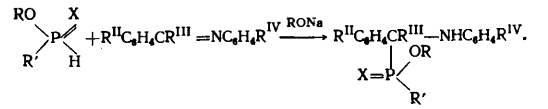
The esters of α-hydroxy-α-phenylalkylphosphonic acids obtained in the reaction of dialkyl hydrogen phosphites with acetophenone and its alkyl derivatives at elevated temperatures in the presence of sodium alkoxides also undergo rearrangement into the corresponding phosphates. As a result of the pyrolysis of the phosphates various derivatives of styrene were obtained in good yields[70]:

$$R''C_6H_4COCH_2R' + (RO)_2P(O)H \xrightarrow{RONa} R''C_6H_4CH(OP(O)(OR)_2)CH_2R' \xrightarrow{\Delta} R''C_6H_4CH=CHR' + (RO)_2P(O)OH.$$

On distilling the products of the addition of dialkyl hydrogen thiophosphites and acid esters of phenylphosphonic acid to acetophenone they were decomposed into the original reagents. Previously, Abramov and coworkers[116] had observed the analogous decomposition of esters of α-hydroxyalkylphosphonic acids obtained from the simplest aldehydes and ketones.

Pudovik and Konovalova think that under the conditions of alkaline catalysis decomposition into the initial reagents and the phosphonate–phosphate rearrangement are competing reactions for esters of α-hydroxyalkylphosphonic acids. The final result depends mainly on the environment of the α-carbon atom. The presence of electronegative substituents at the α carbon atom creates favourable conditions for the phosphonate–phosphate rearrangement to take place.

Pudovik studied the addition of acid esters of phosphorus acids at the C=N bond in the presence of alkaline catalysts, by the example of Schiff bases and the esters of isocyanic acid[87,89,117]:



Kuznetsov and Bakhitov obtained a series of products of the addition of dialkyl hydrogen phosphites to di-isocyanates[118].

Pudovik and Moshkina showed that the addition of dialkyl hydrogen phosphites and dialkyl hydrogen thiophosphites to diazophosphinic esters and tetra-alkyl esters of azodiphosphinic acid takes place at the nitrogen–nitrogen double bond[119].

Dialkyl hydrogen phosphites and dialkyl hydrogen dithiophosphite add to alkene α-oxides to form esters of β-hydroxyalkylphosphonic acids[87] and S-β-hydroxyalkyl esters of dithiophosphoric acids[120]

$$CH_2-CH_2 + (RO)_2P(O)H \longrightarrow HOCH_2CH_2P(O)(OR)_2.$$
$$\quad\ O$$

Opening of the epoxide ring has been established for a series of unsymmetrical α-oxides[121].

B. A. Arbuzov and Vinokurova synthesised a series of bifunctional organophosphorus compounds by the addition of phenylphosphine and butylphosphine to unsaturated compounds containing various functional groups[122]:

$$RPH_2 + 2CH_2=CHR' \rightarrow RP(CH_2CH_2R')_2,$$

where R = C_6H_5, C_4H_9; R′ = CO_2Alk, CH_2OH, CH_2NH_2, CN, etc.

In 1952 Pudovik and Lebedeva effected the addition at the multiple bonds of various unsaturated compounds of the electrophilic type for a series of other phosphorus-containing compounds with a labile hydrogen atom: esters and the nitrile of phosphonoacetic acid, phosphonoacetone[87,123] and subsequently for esters of allylphosphonic acid[124]:

$$CH_2=CH-R + X-CH_2-P(O)(OR')_2 \rightarrow (R'O)_2P(O)CH(X)-CH_2CH_2R$$

where R = $CO_2C_2H_5$, CN, $COCH_3$; X = $CO_2C_2H_5$, $COCH_3$, CN.

Pudovik and coworkers were also the first to study the condensation of phosphonoacetic ester, phosphonoacetone, etc. with aromatic and aliphatic aldehydes, which led to the production of a series of phosphorus-containing alkene derivatives[125]:

$$RCHO + CH_2(X)P(O)(OR')_2 \rightarrow RCH=CX-P(O)(OR')_2 + H_2O,$$

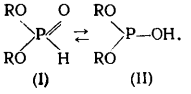
where X = $CO_2C_2H_5$, CH_3CO_2, or CN.

Unsubstituted amides of the dialkyl esters of phosphoric acid are also capable of addition at multiple bonds[126,127]:

$$(RO)_2P(O)NH_2 + CH_2=CHCN \xrightarrow{RONa} (RO)_2P(O)NHCH_2CH_2CN + (RO)_2P(O)N(CH_2CH_2CN)_2.$$

The addition of the anilide of diethyl hydrogen phosphite to the esters and nitriles of unsaturated acids takes place with transfer of the reaction centre and formation of N-phenylimidophosphonates[128].

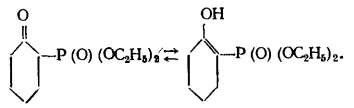
In addition to the study of the reactivity of organophosphorus compounds problems of investigating their structure received considerable attention by the Kazan' scientists. In 1905 A. E. Arbuzov solved the problem of the structure of phosphorous acid and its organic derivatives, which is cardinal for the chemistry of phosphorus[1]. It was shown that all the neutral esters of phosphorous acid and derivatives of phosphorus (III) but that phosphorous acid itself and its acid esters are derivatives of phosphorus(V). On the basis of these investigations, A. E. Arbuzov concluded that compounds with hydroxyl at phosphorus(III) were unstable and similar to alcohols of the vinyl series. Even at that time he recognised the possibility of the existence of tautomeric forms for phosphorous acid itself and for some of its derivatives[77]. Subsequently this question was studied in detail in the example of the dialkyl hydrogen phosphites, the structure of which can be presented by two tautomeric forms:



(I) (II)

The numerous investigations of A. E. Arbuzov and B. A. Arbuzov and their coworkers, and also of several other Soviet and foreign scientists showed that most of the chemical facts and the results of investigations of the dialkyl hydrogen phosphites by physical methods indicate their phosphonate structure although some reactions occur which are difficult to explain without accepting the existence of a tautomeric equilibrium[104]. At the present time it can be taken as proved that the tautomeric equilibrium of the dialkyl hydrogen phosphites is greatly displaced to the side of the phosphonate form (I). As B. A. Arbuzov and coworkers recently showed[129], dialkyl hydrogen phosphites with electronegative substituents at the ester radicals (the cyano-group, chlorine atoms), for which structure (II) can be postulated, are also represented by a structure with a phosphorus(V) atom. Esters of β-ketophosphinic acids formed an interesting subject for the study of tautomeric conversions in the series of organophosphorus compounds. More than once A. E. Arbuzov emphasised the deep analogy between the phosphono-group and the carboxyl group and stated the possibility of the existence of tautomeric forms in compounds of this type[130]. Later B. A. Arbuzov, Vinogradova, and Polezhaeva synthesised a large number of esters of β-ketophosphonic acids and made a systematic investigation with the aim of establishing the presence of tautomerism and of comparing the influence of carboxylic and phosphono-groups for the tendency to give enol forms.

With the aid of chemical and spectroscopic methods of investigation it was shown that phosphonoacetic and methylphosphonoacetic esters, like malonic, do not contain detectable amounts of enol. Phosphonoacetone and methylphosphonoacetone, in distinction from acetoacetic ester, exhibit considerable enolisation only in an alkaline medium[131]. With phosphonoacetophenone the results of the chemical and physical investigations suggest the presence of only insignificant amounts of the enol form[131,132]. Analogous results were obtained also for diphenylacetonylphosphine oxide and diphenylphenacylphosphine oxide[40]. The presence of a considerable amount of the enol form was observed in an ester of 2-oxocyclohexylphosphonic acid—the phosphorus analogue of the ester of 2-oxocyclohexylcarboxylic acid[133]. Titration with bromine in alcoholic medium showed the presence of 9% of the enol, and in hexane medium, of 60% enol:



Only weak enolisation was observed for the diethyl ester of 2-oxocyclopentylphosphonic acid, which accords with the insignificant content of the enol form in the esters of 2-oxocyclopentylcarboxylic acid[134].

On the basis of these results B. A. Arbuzov and coworkers[134] concluded there was a definite analogy in the enolisation of the β-keto-acids and their phosphoric analogues. It was noted, however, that the β-ketophosphonic esters are enolised to a less extent. There is no complete parallel.

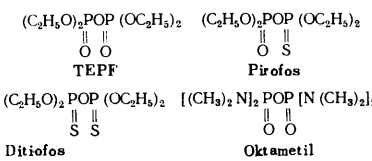
B. A. Arubuzov, Samitov, and Zykova obtained extremely interesting results in studying the structure of organophosphorus compounds by proton magnetic resonance. A large number of investigations in this direction was carried out on a high-resolution NMR spectrograph built in the Research Laboratory for the Structure of Organic Compounds of Kazan' University under the direction of Samitov in 1958–1960.[135] With the aid of the ^{1}H- and ^{31}P-NMR spectra the structure of a series of cyclic compounds of the phospholene type was established, the diastereoisomerism of the oxaphospholenes was studied, and interesting investigations were made into the structure of various types of acyclic esters of phosphoric and phosphonic acids of importance for establishing the mechanism of certain reactions[35,62,67].

In addition to spectroscopy and thermography, B. A. Arbuzov used several other physical methods to study the fine structure of organophosphorus compounds: the parachor method, dipole moments, viscometry, cryoscopy, and polarography[136]. With their aid he studied the problems of the association of molecules of organophosphorus compounds, their intramolecular and intermolecular interactions, and the nature of the arrangement of the alkyl groups and their mutual orientation in the esters of acids of phosphorus. The method of dipole moments was used to show the possibility of free rotation of non-regular groups in the molecules of organophosphorus compounds.

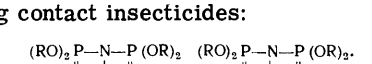
A series of investigations was concerned with compounds which contain an asymmetrical phosphorus atom[137]. In 1929, A. E. Arbuzov and coworkers synthesised certain phosphonic and thiophosphonic acids with an asymmetric phosphorus atom and attempted to resolve them into optical antipodes. Kamai and coworkers synthesised a large number of asymmetric phosphonium derivatives. They succeeded in obtaining two diastereomeric d-π-bromocamphorsulphonates for allylbenzylethylphenylphosphonium bromide. Later Kamai and Usacheva separated the dextrorotatory benzylethylmethyl-p-tolylphosphonium chloride, bromide, and iodide, which exhibit high optical stability. Somewhat earlier, Kumli and coworkers[192] had succeeded in separating into optical antipodes a heterocyclic asymmetric phosphonium salt.

The theoretical investigations in the field of organophosphorus compounds which are being carried out in the Kazan' school of organophosphorus chemistry are closely the Kazan' scientists in the field of the synthesis of physiologically active organophosphorus compounds. As is well known, as long ago as 1932, in studying the reaction of

bromine with sodium diethyl phosphite, A. E. and B. A. Arbuzov were the first to obtain esters of pyrophosphorous and monothiopyrophosphorous acids and to isolate pure esters of hypophosphoric and pyrophosphoric acids[138]. Later Schrader observed that tetraethyl pyrophosphate, its thio-analogue, and several other organophosphorus compounds exhibit strong insecticidal action. From 1946 onwards systematic investigations were carried out in the Chemical Institute of the Kazan' Section of the Academy of Sciences of the USSR in the field of synthesis of new phosphorus-containing insecticides with contact and systematic action. During this period particular attention was paid to derivatives of pyrophosphoric and thiopyrophosphoric acids. In addition to the development of new, simple, and practicable methods of making such highly effective insecticides as TEPF, Pirofos, Ditiofos, Oktametil[139]



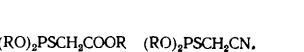
B. A. Arbuzov, Alimov, Nikonorov, Grechkin, Rizpolozhenskii, and others obtained a large number of new mixed esters, ester-amides, and amides of pyrophosphoric and thiopyrophosphoric acids[140]. Neklesova investigated their insecticidal activity and their action on warm-blooded creatures. Among the compounds obtained considerable interest attaches to the mixed ester amides of dithiopyrophosphoric acid, which exhibit pronounced insecticidal action and low toxicity. B. A. Arbuzov and Alimov synthesised a new type of organic derivative of phosphorus with the P–N–P bonding; some of these compounds are rather strong contact insecticides:



The dialkylphosphono-2,2,2-trichloroethyldialkyl phosphates obtained by B. A. Arbuzov and Nikonorov on the basis of chloral approach Pirofos, Ditiofos, and TEPF in their insecticidal action. B. A. Arbuzov and Alimov[140,141] synthesised a series of insecticides with three phosphorus atoms per molecule.

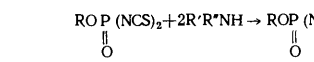
With the aim of obtaining physiologically active organophosphorus compounds the Kazan' chemists synthesised a large number of compounds not previously described in the literature with one phosphorus atom per molecule—esters and amides of phosphoric, thiophosphoric, dithiophosphoric, and [phosphonic] phosphinic acids and various derivatives of them. Strong insecticidal properties were shown by the esters of 1-acetoxy-2,2,2-trichloroethylphosphonic acid, obtained by Nikonorov[142,143]. The dimethyl ester of this acid, which exhibits low toxicity for warm-blooded creatures and good fungicidal properties, was recommended for clinical trials as a substance for the treatment of certain fungal illnesses.

The esters of thiophosphoric acid with alkoxycarbonylmethyl and cyanomethyl radicals acted as active insecticides[140]:

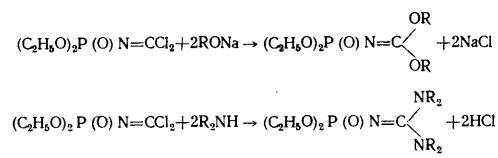


Yarmukhametova and Cheplanova synthesised phosphorus-containing derivatives of pentachlorophenol and pentachlorothiophenol[144].

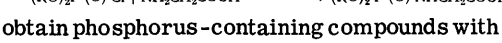
An especially large number of investigations were made in the field of the synthesis of compounds with a phosphorus–nitrogen bond. Alimov and coworkers obtained many new mono- and di-*N*-substituted esters of phosphoramidic acid. Tests showed that dialkyl-*N*-alkoxycarbonylmethyl phosphoramidates are powerful insecticides but rather toxic for warm-blooded creatures[145]. As a result of the addition of secondary amines to the esters of mono- and di-isothiocyanatophosphoric acids Alimov and Levkova synthesised phosphorus-containing derivatives of thiourea[146]:



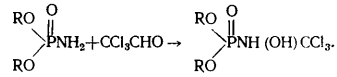
The dichloromethyleneamides of dialkyl hydrogen phosphates obtained by these authors by the action of chlorine on dialkylisothiocyanatophosphates [dialkyl phosphoro(isothiocyanatidates)] are extremely reactive compounds. They were used to synthesise a variety of derivatives of the methyleneamide of diethyl hydrogen phosphate [diethyl *N*-methylenephosphoramidate]: *N*-phosphorylated derivatives of iminocarbonic, iminothiocarbonic, and iminothiocarbamic acids, imidourea, formimine, etc.[147]:



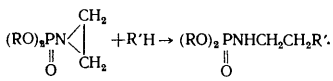
Alimov and coworkers accomplished the *N*-phosphorylation of formamide[148] and of glycine and its derivatives[149]:



To obtain phosphorus-containing compounds with insecticidal or bactericidal activity, Alimov and Antokhina studied the condensation of a series of amides of phosphoric acid and some other organophosphorus compounds with chloral[150]:



Over several years Grechkin and coworkers made a systematic investigation of phosphorus-containing derivatives of ethyleneimine [aziridine], which as the literature indicates can exhibit anti-tumour activity and several other valuable properties. Mono-, di-, and tri-ethyleneamides of phosphoric, phosphorous, and thiophosphoric acids were synthesised[151–153] and it was shown that the ethyleneimine ring substituted at the nitrogen by a phosphono-group is much more stable to the action of various reagents than the free ethyleneimine ring. The addition of a series of compounds with a labile hydrogen atom and of halogens and alkyl halides to mono- and di-ethyleneimides of phosphoric acid was studied in detail, the reaction being given the name *N*-dialkylphosphonaminoethylation:

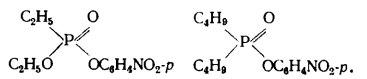


Grechkin and Khamitov obtained some organophosphorus derivatives of azetidine.

B. A. Arbuzov and coworkers synthesised a series of esters of phosphoric and thiophosphoric acids containing heterocyclic radicals. Among those which were powerful insecticides exhibiting comparatively low toxicity towards

warm-blooded creatures were derivatives of pyrimidine and imidouracil[154]. Dialkyl tetrahydrofurfuryl phosphates are rather active as insecticides and exhibit toxic properties[155]. Esters of phosphoric and thiophosphoric acids with pyrazole, α-aminopyridine, carbazole, and certain other radicals were also synthesised.

Razumov and coworkers prepared a large number of organophosphorus compounds with varying ranges of biological action[156,157]. In addition to compounds which exhibit anti-cholinesterase action, products were obtained with spasmolytic and cholinolytic activity. Among those compounds finding a wide use in medical practice and whose action is based on their anti-cholinesterase activity mention must be made of the ethyl *p*-nitrophenyl ester of ethylphosphonic acid (Armin). It is used as an antiglaucomatosic substance which is a hundred times more active than natural pilocarpine. Another strongly-acting antiglaucomatosic drug is *p*-nitrophenyl dibutylphosphinate (Nibufin). It simultaneously tones up smooth muscle, in consequence of which it is used in atonia of the gastrointestinal tract and of other smooth-muscle organs. It is also used with Armin as a parturifacient:



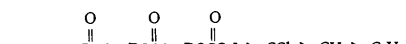
Armin Nibufin

Another antiglaucomatic drug is the tetraethyl monothiopyrophosphate (Fosarbin or Pirofos) first synthesised by A. E. and B. A. Arbuzov and mentioned above as a highly effective insecticide.

Razumov and coworkers also obtained a series of unsaturated esters of dialkylphosphinic acids and of polychlorinated esters of alkylphosphonic acids with antibacterial properties. It has been shown that certain phosphorylated acetals and aldehydes exhibit antivirus activity. Razumov synthesised some extremely interesting organophosphorus compounds with spasmolytic and also potentiating action based on the specific action on the central nervous system. The most active spasmolytics were the esters of diallylphosphinic acid, and of these the isopropyl diallylphosphinate, which is furthermore an antidote for powerful anticholinesterasis poisons—Armin and Nibufin.

B. A. Arbuzov and coworkers[158] synthesised a series of phosphacyclopentenes which exhibit anticholinesterase activity, low toxicity, and pronounced antispasmodic action.

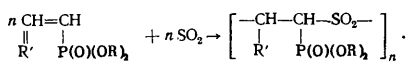
In recent years a new, interesting, and important direction in the chemistry of organophosphorus compounds has evolved—the synthesis of phosphorus-containing monomers and the production of polymers based upon them and exhibiting enhanced resistance to fire, thermal stability, inertness to many chemical reagents, good adhesion to various materials, and other valuable qualities. Several investigations in this field were carried out by the Kazan' scientists. A large number of derivatives of unsaturated phosphinic acids, unsaturated esters of phosphorus acids, various bi-, ter-, and multi-functional phosphorus-containing compounds were synthesised; their reactions were studied: polymerisation, copolymerisation, migration polymerisation, polycondensation, leading to the formation of polymeric products with a phosphorus atom in the principal or side chain. Derivatives of αβ-unsaturated phosphinic acids are of special interest for the synthesis of phosphorus-containing polymers. Kabachnik, Kolesnikov, and their coworkers and several other authors have studied the polymerisation and copolymerisation of esters of vinylphosphinic acids. Pudovik and Kuzovleva obtained solid transparent polymers based on the esters of α-acetoxyvinylphosphonic, α- and β-alkoxycarbonylvinyl- and cyanovinyl-phosphonic acids[159]. Kamai and Tsivunin investigated the ability to polymerise of a series of derivatives of ethylalkenylphosphonic acids[160]. Kuznetsov and coworkers[161] studied the copolymerisation of esters of vinylphosphonic, allylphosphonic, and but-2-en-1,4-bis(phosphonic) acid with acrylic and methacrylic acids. They obtained also a series of polymers of certain unsaturated phosphorus-containing compounds and their copolymers with alkenes, alkadienes, and other monomers on Ziegler-type catalysts[162]. Kamai and Kukhtin investigated the polymerisation of the allyl esters of phosphinic acids in the presence of peroxide initiators[163]. It was shown that the various groups at the phosphorus atom can be arranged in the following series according to the magnitude of their influence on the ability of allyl esters to polymerise:



Kennedy and coworkers[164] later added to this series.

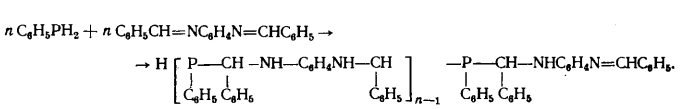
Pudovik and Kashevarova synthesised a large number of organophosphorus monomers which were derivatives of acrylic and methacrylic acids. They obtained phosphorus-containing esters and amides of acrylic and methacrylic acids, mixed anhydrides of acrylic and methacrylic acids, and acid esters of phosphoric, phosphonic, and phosphorous acids. Their polymerisation and copolymerisation gives solid vitreous product, insoluble in organic solvents and exhibiting reduced combustibility[165].

Kuznetsov and Faizullin synthesised a series of organophosphorus polysulphides by the copolymerisation of sulphur dioxide and certain unsaturated phosphorus-containing compounds[166]:

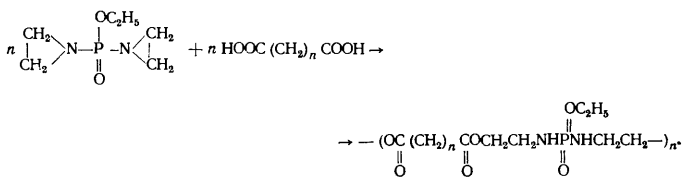


The possibility of hardening liquid organophosphorus polysulphides by reaction with mono- and di-isocyanates has been demonstrated.

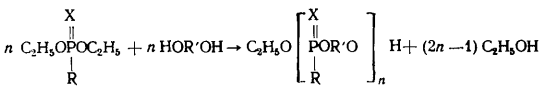
A. N. Pudovik and M. A. Pudovik brought about the migration polymerisation in a series of phosphorus-containing compounds[167]. When acid diphosphites, diphosphinites, and phenylphosphine react with certain organic compounds with two double bonds, polymeric products are formed according to the scheme:



A series of phosphorus- and nitrogen-containing polymeric products was obtained by Grechkin on the basis of the reaction of *N*-phosphonaminoethylation[168]:



Pudovik and coworkers[169,170] used polyester interchange of esters of phosphorus acids with glycols to obtain a series of polymeric products with a phosphorus atom in the main chain—polyalkyleneglycolphosphonates, polyalkyleneglycolethyl(phenyl)phosphinites, polyalkyleneglycol-phosphorothiolates and -phosphorothiolothionates[169,170]:



where R = Alk, C_6H_5, SH; and X = O or S.

The products of the addition of polyalkyleneglycol-phosphorothiolothionates to certain unsaturated electrophilic reagents exhibit insecticidal properties and are distinguished by considerable duration of the action under natural conditions. Phosphorus-containing polyesters were also obtained by the homopolycondensation of esters of hydroxymethylphosphonic acid[171] and in the reaction of the di(acid chloride) of 4-chlorobut-2-enphosphonic acid with dihydroxy-compounds.

Kuznetsov and Shermergorn and their coworkers synthesised polyphosphites based on alkyl(or aryl) phosphorodichloridites and diphenols, and studied in detail the properties of the polymers formed[172]. On the basis of the polycondensation of tetra(hydroxymethyl)phosphonium chloride, tri(hydroxymethyl)phosphine, di(hydroxymethyl)-phosphonic acid, and bis-2-carboxyethylphosphinous acid with various bifunctional organic compounds, Kuznetsov and coworkers synthesised phosphorus-containing polyesters and polyamides which are incombustible resins and in several instances capable of hardening[173,174]. A series of organophosphorus polysulphonates has also been obtained[175]. Kuznetsov and Khairullin have developed methods for the synthesis of phosphorus-containing Thiokols [polysulphide rubbers (Ed. of Translation)].

The phosphorylation of organic high-molecular-weight compounds has been used increasingly in recent years for the production of phosphorus-containing materials. A. E. Arbuzov and Alimov were the first to phosphorylate cellulose. Pudovik and coworkers synthesised a series of phosphorus-containing polymers on the basis of the addition of acid esters of phosphorus acids to unsaturated polyesters and poly(Schiff bases).[176] A graft copolymer of cellulose and 1-(diethyl phosphono)ethyl methacrylate has been obtained.

Kuznetsov and Devitaeva have phosphorylated polyethylene with phosphorus acid chlorides[177].

Kirpichnikov and coworkers have completed important investigations on the use of organophosphorus compounds for improving the properties of polymeric materials[178]. It has been shown that alkylaryl esters of pyrocatechol-phosphorous acid are good stabilisers for several polymers. The variation of inhibiting action with structure of organophosphorus compounds has been studied. Certain di- and poly-phosphites have also been shown to exhibit high stabilising properties[172,178].

In several papers and patents the Kazan' scientists have described phosphorus-containing plasticisers for tri-acetate cinematographic film base[179] and catalysts for the synthesis of carbodi-imides[180], have carried out the synthesis of extractants, and have found that oxidative phosphorylation can be used to obtain certain products based on petroleum alkanes which are interesting practically[181].

As it is impossible to give a complete list of the works of the Kazan' scientists in the field of the chemistry of organophosphorus compounds, we list only references to the most important papers, review articles, and also the first and last works of individual series.

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αβ-UNSATURATED ETHERS AND THEIR ANALOGUES IN REACTIONS OF DIENE SYNTHESIS

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1. INTRODUCTION

αβ-Unsaturated ethers, such as simple vinyl ethers, cyclic unsaturated ethers of the dihydrofuran and dihydropyran type, alkoxydienes, and alkoxyacetylenes, represent a special group of unsaturated compounds as regards their combination of chemical properties. Similar properties are possessed by their sulphur analogues, the αβ-unsaturated sulphides, and by ketens. The compounds of this group are distinguished by high reactivity in a variety of conversions which proceed by an ionic mechanism, mainly with electrophilic reagents. From the standpoint of chemical structure these compounds are distinguished by the presence at the double bond of an electron-donating substituent (–OR or –SR), which determines the special nature of the polarisation of the double bond.

The most characteristic representatives of this group of compounds are the vinyl ethers, in the properties of which appear most distinctly and uniquely the fundamental features of the chemical properties and structure possessed by the unsaturated ethers and their analogues.

Among the reactions of the vinyl ethers which take place by an ionic mechanism are hydrolysis, addition of alcohols and organic acids, hydrogen halides and halogens, polymerisation and copolymerisation. Most of the reactions of vinyl ethers are catalysed by mineral acids and by Lewis acids, that is, by electrophilic reagents. At the same time they are completely stable to the action of nucleophilic reagents—alkalis. Vinyl ethers do not react with alkali metals[1]. Many reactions which proceed by a radical mechanism are not characteric for alkyl vinyl ethers. In sharp contrast to the ease with which ionic (cationic) polymerisation of alkyl vinyl ethers takes place is their passivity in radical polymerisations[2–5]. Schildknecht and coworkers[4], who made a comparative study of the polymerisation of various unsaturated compounds, divided them into three groups according to the type of

TABLE 1. Classification of the alkene monomers by polarisability type.

First group	Second group	Third group
2-Methylprop-1-ene	styrene	ethylene
Methylbutene	butadiene	vinyl halides $CH_2=CHX$
α-Methylstyrene	divinyl ether	vinylidene dihalides $CH_2=CX_2$
2-Isopropenyltoluene	methyl vinyl ketone	vinyl esters $CH_2=CHOCOR$
Alkyl vinyl ethers	*N*-vinylpyrrolidone	acrylic esters
Methyl vinyloxyacetate $CH_2=CH-O-CH_2COOCH_3$	*N*-vinylcarbazole	methacrylic esters

polymerisation (Table 1): first group—compounds which polymerise by an ionic mechanism under the action of Friedel-Crafts catalysts at low temperatures but which do not give the usual high-molecular-weight polymers in free-radical or thermal polymerisation; second group—those which polymerise by both an ionic and a radical mechanism; third group—compounds which polymerise by a radical mechanism and give high-molecular-weight polymers in peroxide or thermal polymerisation.

Even by the above criterion alkyl vinyl ethers are sharply distinguished from unsaturated compounds which contain at the double bond such electron-acceptor substituents as carbonyl, carboxyl, an acyloxy-group, halogen, etc. which enter into the third group. In one group with the alkyl vinyl ethers are certain unsaturated compounds which contain electron-donor substituents at the double bond. The existence of an intermediate group of unsaturated compounds is natural. According to polymerisation type, the intermediate group includes not only divinyl ether but also aryl vinyl ethers and alkoxy-dienes, which are capable of both ionic and radical polymerisation[6,7], to which, however, all the ionic reactions of alkyl vinyl ethers are inherent. In addition to high reactivity in relation to various electrophilic reagents, in which they show complete similarity with alkyl vinyl ethers, acetylenic ethers also react with nucleophilic reagents, for example, with amines, by forming addition products at the triple bond[8,9]. Evidently this can be explained by a breakdown in the symmetry of the electron cloud of the carbon atom in the formation of a triple bond and by the exposure of a positive charge, which makes nucleophilic attack possible[10].

In vinyl sulphides, the properties of which are in many respects analogous to those of vinyl ethers, the presence of a sulphur atom brings about a series of peculiarities, which are expressed, in particular, in a duality in their properties, and in a greater variety of chemical conversions. In polymerisation type these compounds can evidently be assigned to the second group, since they readily polymerise by both an ionic and a radical mechanism[11]. Furthermore, the vinyl sulphides generally show considerable activity in radical reactions[12]. Many ionic reactions of keten are extremely close in nature to the reactions of alkyl vinyl ethers[13].

The reaction with acetals discovered by Müller-Cunradi and Pieroh[14] which proceeds by an ionic mechanism is especially specific for αβ-unsaturated ethers. This reaction has now been studied well[15,16] and it has been shown that a great variety of αβ-unsaturated ethers and sulphides, as well as keten, react with acetals[13]. Nevertheless unsaturated compounds with electron-withdrawing substituents, for example, the compounds of the third group in Table 1, which are generally distinguished by high reactivity, were completely incapable of condensing with acetals.

The behaviour of αβ-unsaturated ethers in the reactions of diene synthesis is highly specific. This appears most sharply in the diene condensations with Schiff bases[17-19]. These reactions serve as yet another criterion for the separation of αβ-unsaturated ethers and sulphides into a special group of compounds. Consideration of the behaviour of αβ-unsaturated ethers in diene condensations with a different type of dienophiles allows certain conclusions to be drawn concerning the mechanism of diene synthesis in general.

At the basis of the specifics of chemical properties of the αβ-unsaturated ethers lies a feature of their structure, the investigation of which has been investigated in a series of special physicochemical and spectroscopic studies. Especially interesting results were obtained recently in studying the infrared and NMR spectra of these compounds.

2. STRUCTURE OF THE αβ-UNSATURATED ETHERS AND THEIR ANALOGUES

A feature of the structure of the αβ-unsaturated ethers and their sulphur analogues is the presence of an –OR or –SR group at a double bond. According to the theory of electron displacement[20,21] the –OR and –SR groups exhibit a negative induction effect ($-I_S$), but less than, for example halogen atoms. This is shown clearly from Table 2, which gives the dissociation constants of substituted acetic acids[22]. In accordance with the lower electronegativity of the sulphur atom in comparison with the oxygen atom the –SR group has a smaller induction effect than the –OR group.

On the other hand, the –OR and –SR groups exhibit a positive mesomeric effect ($+M$), greater than the halogen atoms. The mesomeric effect of the –SR group is less than that of the –OR group, in accordance with the rule[20,21] by which within the limits of a given group of the Periodic System the higher the atomic number the less the tendency to form double bonds. The above two factors should evidently determine the static state of the electrons of the double bond of unsaturated ethers and sulphides. Finding the relation of these two effects is of considerable importance.

The orientation of ionic addition of various reagents to αβ-unsaturated ethers leads to the conclusion about the presence of an excess of negative charge at the β-carbon atom. On this basis it could be assumed that on the negative induction effect of the –OR group in these compounds is superposed a positive mesomeric effect and that as a whole this group is an electron donor:

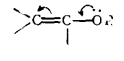


TABLE 2. Dissociation constants of substituted acetic acids.

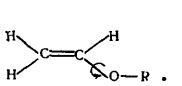
Acid	K
CH_3COOH	$1.855 \cdot 10^{-5}$
CH_3S-CH_2COOH	$1.92 \cdot 10^{-4}$
$C_2H_5O-CH_2COOH$	$2.50 \cdot 10^{-4}$
CH_3O-CH_2COOH	$2.94 \cdot 10^{-4}$
$Cl-CH_2COOH$	$1.55 \cdot 10^{-3}$

In recent years the investigation of the NMR spectra of a series of unsaturated ethers has allowed direct proof to be obtained of the existence of increased electron density at β-carbon atoms due to the mesomeric effect of the –OR group, which is expressed in the conjugation of the unshared electron pair of the oxygen atom with the π-electrons of the double bond. Analogous results were also obtained for unsaturated sulphides. Investigation of the ultraviolet and infrared spectra and heats of hydrogenation also suggest the presence of $p-\pi$-conjugation.

In the NMR spectra of alkyl vinyl ethers[23-25] an extremely large chemical shift has been observed for β-protons to the side of higher fields (75–85 Hz) in comparison with ethylene[26]. It has been shown[25] that this effect cannot be due to the anisotropy of the oxygen atom but is the consequence of conjugation of the unshared pair of the electrons of the oxygen atom with the unsaturated system. In methyl vinyl sulphide the shift for the β-protons is considerably less (14–28 Hz). Were the chemical shift of the protons due to the inductive effect of the oxygen and sulphur atoms the picture should be reversed. The observed difference in the chemical shift of the β-protons is explained by the difference in the degree of $p-\pi$-conjugation of the oxygen and sulphur atoms, which is more significant for oxygen. For α-protons the observable difference in the chemical shift corresponds to the order of electronegativity of the oxygen and sulphur atoms. The chemical shifts in methyl vinyl and butyl vinyl ethers are almost the same. Group R does not significantly affect the β shift and evidently does not change the degree of $p-\pi$-conjugation of the oxygen. The oxygen atom acts as a buffer between group R and the double bond. In isopropenyl methyl ether the methyl group decreases the total shift of the two β-protons by 16 Hz, which is considerably below the effect of the methyl group in propene, where there is a general shift of the β-protons by 30 Hz in comparison with ethylene.

Interesting results[27] were obtained in investigating the NMR spectra for the series of substituted ethylenes $CH_2=CHX$, where X = H, CH_3, Cl, OCH_3, CN, and C_6H_5. The existence of a linear relation between the chemical shift of the β-protons and the group dipole moments of substituents X was demonstrated. Parallel curves were obtained for *cis*- and *trans*-β-protons. The results for methyl vinyl ether (X = OCH_3) fit into this relation if it is assumed that the group OCH_3 as a whole is positive in relation to ethylene (dipole moment +1.16 D). This is analogous to *p*-chloroanisole, in which the group dipole moment of the chlorine atom and the OCH_3 group are added together.

Investigation of the vibrational spectra (infrared and microwave) of alkyl vinyl ethers showed that they have a series of features connected with the direct proximity of the ethereal oxygen to the double bond[28-31]. In the region of the C=C stretching vibrations in the spectra of alkyl vinyl ethers the presence of three absorption bands is noted, at 1642 cm^{-1}. On the basis of a consideration of the published data and additional experimental investigations it was shown[28,29] that the presence of these bands is connected with the realisation of rotation isomers:



On the basis of the microwave spectra the difference in the energies of the rotation isomers for butyl vinyl ether was determined. The vibrational spectrum of methyl vinyl ether was investigated in detail[29]. The results of the investigations suggest that the rotation isomers which arise differ in the degree of interaction of the π-electrons of the double bond with the unshared electron pair of the oxygen atom. The bathochromic shift of the absorption band of the double bond of alkyl vinyl ethers which is observable in their ultraviolet spectra[32] (absorption band in the region 1900–2000 Å) in comparison with the double bond of alkenes (absorption band at 1800 Å) can be explained by conjugation. The results of an investigation of the spectra of vinyl sulphides[33] also show the existence of interaction of the sulphur atom with the double bond.

Kistiakowsky and coworkers[34] determined the value of the heat of hydrogenation of certain unsaturated compounds including several vinyl ethers (Table 3). The results obtained show that there is considerable conjugation of CH=C–O–C. This conclusion follows from the heats of hydrogenation of the alkyl vinyl ethers having a mean value between the heats of hydrogenation of unconjugated double bonds, for example, in allyl alcohol, and the heats of hydrogenation of the double bond having an aromatic nature, for example, in furan.

The results of Doliver and coworkers[34] were recently confirmed by calculation of the heat of hydrogenation from measured heats of combustion[35]. The heats of combustion of ethyl vinyl and divinyl ethers compared with the heat of combustion of diethyl ether are:

$$\Delta H^\circ_c \text{ (diethyl ether, } g) = -657.52 \pm 0.18 \text{ kcal mole}^{-1},$$
$$\Delta H^\circ_c \text{ (ethyl vinyl ether, } g) = -615.98 \pm 0.22 \text{ kcal mole}^{-1},$$
$$\Delta H^\circ_c \text{ (divinyl ether, } g) = -578.14 \pm 0.19 \text{ kcal mole}^{-1}.$$

The authors state that conjugation in ethyl vinyl ether is slightly higher than in divinyl ether.

The dipole moments of vinyl ethers[36] (Table 4) differ little from those of the corresponding saturated ethers. Evidently, in the present instance they cannot give any information about the degree of polarisation of the double bond.

Ketens are analogues of the vinyl ethers in the sense that they also contain an oxygen atom at a double bond and in them, just as in the vinyl ethers, conjugation of the unshared electron pair of the oxygen atom with the π-electrons of the double bond is possible, as Ingold first stated[37]. Determination of the dipole moments of the transition in ketens showed that they are considerably (30–40%) lower

TABLE 3. Heats of hydrogenation of unsaturated compounds.

Compound + xH_2	Heat of hydrogenation $\Delta H_{298.0K}$, kcal $mole^{-1}$
$CH_3-C(OC_2H_5)=CH_2+1H_2$	−25.101±100
$CH_3-C(OCH_3)=CH-CH_3+1H_2$	−24.797±200
$C_2H_5O-CH=CH_2+1H_2$	−26.740±60
$CH_2=CH-O-CH=CH_2+2H_2$	−57.236±100
 $+2H_2$	−36.630±120
$CH_2=CH-CH_2OH+1H_2$	−31.45±300

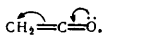
TABLE 4. Dipole moments ($\times 10^{18}$) of the ethers and their analogues.

Compound	Vapour, D	Solution, D
$CH_3—O—CH_3$	1.29	—
$C_2H_5—O—C_2H_5$	1.16	1.22
$C_2H_5—O—C_4H_9$	—	1.20
$CH_2=CH—O—CH=CH_2$	—	1.06
$CH_2=CH—O—C_4H_9$	—	1.25
$CH_2=CH—O—iso\text{-}C_4H_9$	—	1.20
$CH_2=CH—O—C_2H_5$	—	1.19
$HC\equiv C—O—C_2H_5$	—	1.98
$HC\equiv C—O—C_4H_9$	—	2.03
$CH_2=CH—S—CH=CH_2$	—	1.20
$CH_2=C=O$	—	1.45 (gas)
$(CH_3)_2C=C=O$	1.85	—
$(C_6H_5)_2C=C=O$	1.90	—

than in the corresponding ketones[38]. The authors gave the explanation that the effect normal for ketones



is weakened (but not extinguished) by the competing mesomeric effect



Spectrometric studies of keten[39] show the presence of an excess of negative charge at the β-carbon atom.

In the presence of an increased electron density at the β-carbon atom at the double bond, that is, the presence of a nucleophilic centre, $\alpha\beta$-unsaturated ethers and their analogues are distinguished from other types of unsaturated compounds in which the substituents at the double bond have an electron-withdrawing character. On comparing $\alpha\beta$-unsaturated ethers with vinyl halides in which p-π-conjugation is also possible, in the latter it evidently does not appear to the same extent and does not predominate over a more significant induction effect.

The nucleophilic nature of the double bond of $\alpha\beta$-unsaturated ethers explains their high reactivity in relation to electrophilic reagents and the inertness to the action of nucleophilic reagents.

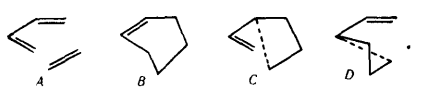
3. MECHANISM OF DIENE CONDENSATIONS

It has now become evident that many of the reactions of diene synthesis which unite the general scheme of addition of a dienophile in the 1,4 position to a diene system cannot be ascribed to any single mechanism both from the viewpoint of the order of combination of the reagents (single- or two-stage) and from the viewpoint of the type of transition of the electrons (homolytic or heterolytic)[40,41]. In support of the single-stage mechanism of a series of diene condensations there are the low values of the pre-exponential factors in the equations for the rate constants of the reactions, approximately 10^{-5}–10^{-6} times the usual rates of collision in gas reactions. In other words, the reactions are characterised by a high negative entropy of activation, which shows that to effect the reactions extremely specific orientation of the reacting molecules is necessary, for example, collision at two points.

In complete agreement with the single-stage mechanism are results[42] which show that acyclic dienes (butadiene) are capable of participating in a diene condensation only after isomerisation into a cisoid conformation. The observance in diene condensations of the principle of *cis*-addition of reagents is also more understandable in single-stage conversion. The mechanisms of the two-stage formation of addition products should provide for additional factors which exclude the possibility of rotation in the product of the first stage of addition[43].

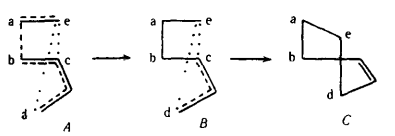
At the same time there are individual instances of diene condensations in respect of which a two-stage mechanism has been established. For example, determination of the change in volume in the formation of a transition state ($\Delta v^{\neq}$) in the dimerisation of isoprene[44] and the diene condensation of 2,3-dimethylbutadiene with butyl acrylate[45] suggested that these reactions are two-stage. It appeared that the transition state is characterised by a significantly greater volume than the reaction products. A single-stage mechanism for the dimerisation of cyclopentadiene was confirmed by the same method[45,46].

According to contemporary views, diene condensations which are stereospecific proceed by the approach of the diene and dienophile molecules which are in parallel planes. The formation of new bonds starts with the overlap of the orbitals of the π-electrons. For a single-stage diene synthesis according to Wassermann[47] the transition state is expressed by a set of resonance structures. For example, structures *A*, *B*, *C*, and *D* represent the transition state for the reaction of butadiene with ethylene:



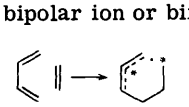
For more complex molecules which contain polar substituents structures which take into account the interaction of specified substituents with unsaturated systems also enter into the transition state.

According to Woodward and Katz[43] the transition state for a two-stage stereospecific diene synthesis can be represented as:



This scheme represents the two-stage mechanism when conversion $B \rightarrow C$ requires an energy of activation. Here the bonds *ed* and *ec* are formed by secondary forces—electrostatic, electrodynamic, and partly exchange forces. When the stage $B \rightarrow C$ of the conversion does not require an energy of activation the bonds *ed* and *ec* are partial and the mechanism stated becomes indistinguishable in practice from a four-centre mechanism.

For a non-stereospecific diene synthesis, transition states of the bipolar ion or biradical type are possible:



There are also contradictory information and opinions concerning the type of electron transition in reactions of diene synthesis. The reactions of the classical diene synthesis (with hydrocarbon diene systems and dienophiles) evidently cannot be related to the heterolytic in external characteristics, since it was shown that the values of the

rate constants and parameters in the Arrhenius equations are almost the same both in the gas phase and in non-polar solvents[40,41]. Moreover, the ideas about heterolytic processes do not agree in many instances with the structural directionality of these reactions[48]. However, it is impossible to classify them as radical reactions, as it was found that they are not catalysed by peroxides[40,41].

Wassermann[47] states that since electrons are indistinguishable there is no sense in speaking of a heterolytic or homolytic transfer of electrons in a four-centre mechanism.

In the mechanism of Woodward and Katz[43] it was assumed that the spins of all the electrons included in the process remain paired all the time. The production of a triplet state under conditions of stereospecific diene synthesis is not very probable[49].

However, it must be noted that the available information on the mechanism of the diene synthesis relates almost exclusively to hydrocarbon dienes and dienophiles. Other types of conversions cannot be ruled out for heterodienes and heterodienophiles, in particular, conversions through bipolar or biradical transition states. Thus, Japanese investigators[50] propose a transition state in the form of a bipolar mesomeric ion for the reaction of octyl vinyl ether with substituted cinnamaldehydes. Henecka[51] states that the formation of ascaridol from α-terpinene and oxygen is a radical reaction. Some authors consider that diene condensations can be brought about by the transfer of electrons into a non-planar six-membered complex, both heterolytically[52,53] and homolytically[51]. We note that apropos of reactions of diene synthesis with hydrocarbon dienes and dienophiles Ingold writes[40] that they proceed predominantly homolytically.

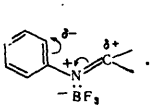
Undoubtedly, for the stereospecific diene synthesis with participation of $\alpha\beta$-unsaturated ethers a tendency to heterolytic transfer of electrons should be more characteristic, considering the unequivocal structural directionality of these reactions and the general uncharacteristic nature of homolytic conversions for this type of dienophile. For example, the condensation of oxygen-containing heterodienes, such as $\alpha\beta$-unsaturated aldehydes, with vinyl ethers always takes place in the same way structurally in accordance with the polarity of the reagents[54,55]. These reactions, moreover, are characterised by the great ease with which they take place and the very high yields of addition products (up to 85%). Alkyl vinyl ethers react with great difficulty with dienes which tend to react preferably by a homolytic mechanism (such as cyclopentadiene)[56]. In their turn these oxygen-containing heterodienes form addition products in very low yields (3–9%) with dienophiles which contain electron-withdrawing substituents at the double bond and tend to radical conversions (such as vinyl acetate, methyl acrylate, methylallyl alcohol, etc.)[57]. Moreover, these condensations proceed structurally despite the polarity of the reagents. Thus the condensation of acrylaldehyde with methyl acrylate leads not to dihydro-3-methoxycarbonylpyran, as might have been expected from the polarity of the reagents, but to dihydro-2-methoxycarbonylpyran. This course of the reaction is explained by the principle of the conjugation of oxygen atoms in the formation of the transition state.

As is well-known, in those instances when the formation of stereoisomers is possible diene condensations proceed stereospecifically with the preferential formation of *endo*-addition products. This was shown by the example of the condensation of cyclopentadiene with maleic anhydride[58,59]. To explain the preferential formation of *endo*-addition products, the principle of the accumulation of multiple bonds in the orientation of reagents in the transition state was advanced. The essence of this principle, which was given quantitative expression in the works of Mousseron and coworkers[60], together with the principle of the conjugation of oxygen atoms (or in the more general form, the principle of the conjugation of unshared electron pairs) is that there are factors other than the polarity of the reagents which are capable of the formation of the transition state. Consideration of the many results on the diene condensation suggests that such a factor can be the general state of charge of the diene system and of the double bond of the dienophile. The action of this factor facilitates the approach of the reagents but does not determine the structural and steric orientation of the components.

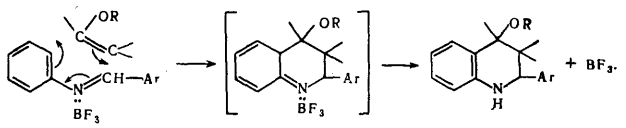
Thus in many of the reactions of classical diene synthesis a diene which does not contain electron-withdrawing substituents is an electron-donor component in relation to the dienophile, whereas the dienophile serves as an acceptor of electrons. This has been confirmed recently by special investigations.

For example, Konovalov[61] studied the reactivity of a series of vinyl and isopropenyl dienophiles which contain electron-withdrawing substituents in reactions of diene synthesis with 2,3-dimethylbutadiene and cyclopentadiene. It was found that the reactivity of these dienophiles increased with decrease in the electron density at the double bond of the dienophile, which was determined as a function of the β-proton chemical shift in the NMR spectrum.

However, as was shown recently[62], there are diene condensations with a reversal of the electronic properties of the components, that is, when the diene serves as the electron-withdrawing component and the dienophile as the electron donor. From this viewpoint the behaviour of alkyl vinyl ethers in the diene synthesis is interesting. Since the double bond of vinyl ethers exhibits a clearly expressed nucleophilic nature, which appears especially sharply in alkyl vinyl ethers, their reactions with dienes should take place the easier the more electron-withdrawing the diene system, and contrariwise will be hindered in electron-donating diene systems. As will be clear from what follows, this position is observed for all the known examples of diene condensations with participation of alkyl vinyl ethers. In addition, such an approach makes it possible to understand the catalysis by Lewis acids of diene condensations of unsaturated ethers and their analogues with Schiff bases[17–19]. As was shown, in the absence of catalysts Schiff bases do not react with unsaturated ethers. And this is understandable, since the quasidiene system formed in this instance by the double bond of the benzene ring and the azomethine group is electron-donating, thanks to the presence of the nitrogen atom. At the same time there are results[63] showing that the diene systems C=C–N=C in oxazoles are capable of reacting with such electron-withdrawing dienophiles as maleic anhydride. In the presence of Lewis acids iminium salts are formed, as was shown[18] by the example of the complex of benzylideneaniline with BF_3. It can be assumed that in this there is strong polarisation of the double bonds:



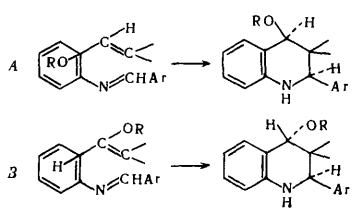
However, besides the above polarisation of the bonds which determine the structural orientation of the components an important factor is that the diene system mentioned acquires electrophilic properties to a high extent. Thanks to this the nucleophilically unsaturated ethers and their analogues react extremely readily with such systems. The reactions begin at room temperature and proceed with considerable evolution of heat giving high yields of addition products:



In addition to conferring electron-withdrawing properties on a diene system a catalyst plays yet another important part. It is already known that to carry out a diene condensation the diene system should have a planar configuration[36]. Moreover it was found[64,65] that in Schiff bases the amine ring is turned through an angle of ~ 60° relative to the plane of the rest of the molecule. This is explained by the competing interaction of the π-electrons of the azomethine group ($\pi-\pi$-conjugation) and the unshared pair of electrons of the nitrogen atom ($p-\pi$-conjugation) with the π-electrons of the aromatic amine ring. During quaternisation of the Schiff base the unshared electron pair is blocked as a result of which it becomes possible to realise the planar configuration of the molecule necessary for the reaction to take place.

Usually only one addition product, or predominantly one, is formed as a result of the condensation. This shows that the reaction is stereospecific.

The structural directionality of the reaction is always determined unambiguously by the polarity of the reagents. The possibility of stereoisomerism under the conditions of single-stage diene synthesis is connected with the different types of orientation of the reagents in the transition state (*A* or *B*):



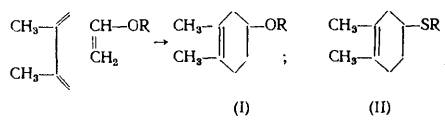
If it is assumed that orientation *A*, corresponding to the principle of the accumulation of unsaturation and unshared electron pairs, is pre-eminent, then the addition products formed predominantly must be considered to be the *cis*-isomers. This also agrees with the observed dependence of the ratio of the isomers on the reaction temperature[19].

Hence the reaction of unsaturated ethers with Schiff bases, which is a new type of diene condensation, is one of the extreme instances of the combination of the electron structures of the dienophile and a diene, namely, the instance when the dienophile exhibits clearly expressed nucleophilic properties and the diene system is electron-withdrawing to a high degree.

4. REACTIONS WITH HYDROCARBON DIENES

Diene systems which do not contain electron-withdrawing substituents exhibit increased electron-donating properties as has been shown by many examples of the reactions of diene synthesis, where they emerge as electron-donating components. Reactions with such dienes evidently have a predominantly homolytic character, which first and foremost relates to dienes not containing strongly polarised double bonds with substituents of electron-donating nature. Dienes such as butadiene, isoprene, 2,3-dimethylbutadiene, etc. easily form addition products with dienophiles containing electron-withdrawing substituents, the double bond in which has a diminished electron density. Thus butadiene and 2,3-dimethylbutadiene form addition products with maleic anhydride in quantitative yields even at room temperature[66].

There are very few examples of the reaction of vinyl ethers with the above hydrocarbon dienes. Apparently, alkyl vinyl ethers are generally incapable of giving addition products with many of these. This can be judged from the fact that in those instances when addition products were obtained, very severe conditions were used and the yields of the addition products were low. Thus, Shostakovskii and coworkers[67] carried out a diene synthesis of n-hexyl vinyl, cyclohexyl vinyl, and phenyl vinyl ethers with 2,3-dimethyl-1,3-butadiene. When the reagents were heated at 220–235°C for 10–12 h addition products were obtained—derivatives of 3,4-dimethylcyclohex-1-ene (I):

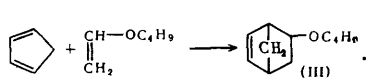


where (I) R = n-C_6H_{13}, C_6H_{11}, C_6H_5; (II) R = C_2H_5, C_6H_5.

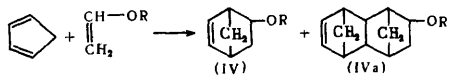
With n-hexyl vinyl ether the yield of addition product was 33.3%. Cyclohexyl vinyl ether (yield of addition product 43.3%) and phenyl vinyl ether (yield of addition product 47%) are somewhat more active. n-Decyl vinyl ether did not give an addition product. Analogous products (II) were obtained with ethyl vinyl sulphide and phenyl vinyl sulphide under milder conditions (175°C, 12 h and 180–185°C, 15 h), the yields being 38.2 and 27.4% respectively.

One of the most active dienes in the reactions of classical diene synthesis is cyclopentadiene, the structure of the molecule of which favours the formation of the transition state. In reactions of diene synthesis cyclopentadiene acts as a donor of electrons. This can explain the extreme ease of reactions with dienophiles which exhibit an electron-withdrawing double bond. For example, methyl vinyl ketone condenses with cyclopentadiene with liberation of heat, by forming an addition product in quantitative yield[68]. On the other hand, alkyl vinyl ethers, as nucleophilic dienophiles, have very weak activity in relation to cyclopentadiene. Reactions take place under severe conditions and give insignificant yields of addition products; in several instances addition products are not formed in general.

Plate and Meerovich[68] first condensed butyl vinyl ether with cyclopentadiene by heating a mixture of the reagents at 200°C for 15 h. This gave 5-butoxybicyclo[2,2,1]hept-2-ene (III) in only 10% yield;

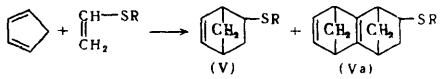


Subsequently Shostakovskii and coworkers[53,69-71] studied the condensation of a series of vinyl ethers with cyclopentadiene. As was shown, the reaction with alkyl vinyl ethers is more difficult and necessitates heating at 180–195°C for 15 h. Under these conditions ethyl vinyl ether did not give an addition product at all and addition products were obtained in low yield from butyl vinyl and cyclohexyl vinyl ethers. Aryl vinyl ethers form addition products in high yields under somewhat milder conditions (heating at 160–170°C for 13 h). It has been found that in the reaction in addition to mono-addition products—ethers of 5-hydroxybicyclo[2,2,1]hept-2-ene (IV)—an insignificant quantity of bis-addition products (IVa) is formed:



where R = C_4H_9, C_6H_{11}, $C_{10}H_{17}(\beta)$; C_6H_5, C_6H_4-t-C_4H_9.

For aryl vinyl ethers the total yield of the mono- and bis-addition products reached 95%. Vinyl sulphides also give addition products more readily than alkyl vinyl ethers[53,72], derivatives of 5-mercaptobicyclo[2,2,1]hept-2-ene (V) being formed, as well as bis-addition products (Va)



where R = C_2H_5, C_4H_9, C_6H_5.

Heating at 160–165°C for 12 h leads to the formation of a mixture of mono- and bis-addition products with a total yield of 72–80%.

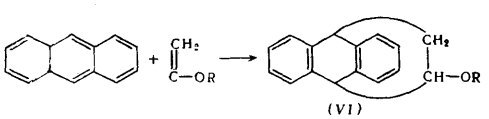
Earlier Alder and coworkers[73] obtained an addition product of cyclopentadiene with *p*-tolyl vinyl sulphide. Prilezhaeva and coworkers[74] state that ethyl vinyl sulphide did not give an addition product with cyclopentadiene at 110°C.

It has been reported[62] that the cyclic unsaturated ether 2,3-dihydrofuran does not form addition products with cyclopentadiene and 9,10-dimethylanthracene.

Shostakovskii and coworkers[71] showed that the reaction of vinyl ethers is stereospecific. In several instances they isolated two isomeric addition products, evidently corresponding to the *endo*- and *exo*-orientation of the reacting components, and showed that their ratio varied with the temperature.

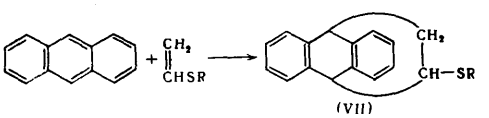
Anthracene, the central ring of which contains an active diene system, reacts rather readily with electron-withdrawing dienophiles. Thus, on boiling anthracene and maleic anhydride in benzene for 3 h, an addition product was obtained in 96% yield[66].

Shostakovskii and coworkers[75] studied the reaction of a series of vinyl ethers and sulphides with anthracene, at 220–240°C for 13–15 h. Phenyl vinyl ether was the most active. At higher temperatures the reaction products resinified, and at lower temperatures the reaction was retarded. Under these conditions addition products (VI) were obtained in yields from 66 to 90% on the anthracene participating in the reaction:



where R = C_4H_9, C_6H_{13}, C_6H_{11}, C_6H_5, *m*-$C_6H_4CH_3$, $C_{10}H_{21}$, $C_{10}H_{17}(\beta)$, and $C_{10}H_7(\beta)$.

Condensation of anthracene with vinyl sulphides under analogous conditions at 180°C gave addition products (VII) in yields of ~ 65% on the anthracene undergoing reaction:

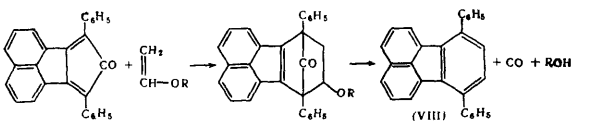


where R = C_2H_5, C_6H_5.

Hence here also the electron-donating properties of vinyl ethers and sulphides hinder the reaction of diene synthesis. Note that the authors give the yields of (VI) and (VII) on the anthracene entering into the reaction. Evidently the yields are considerably less than theoretical. For example, for n-hexyl vinyl ether the experimental results show that the yield of addition product is 46% of theoretical, whereas the yield on the anthracene entering into the reaction was 77.6%.

5. REACTIONS WITH SUBSTITUTED HYDROCARBON DIENES

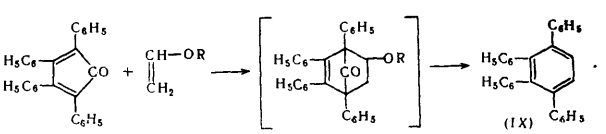
Abramov and coworkers[76-78] studied the reaction of a series of vinyl ethers with various cyclones. These are dienes which contain an electron-withdrawing substituent (the C=O group). The presence of this group should diminish the nucleophilic nature of the diene system, possibly conferring on it to some extent an electrophilic nature. Actually, with electrophilic dienophiles such as maleic anhydride cyclones do not react as readily as cyclopentadiene. The reaction of cyclopentadiene with maleic anhydride starts at room temperature and is exothermic[79,80]. With a cyclone rather prolonged heating of the mixture of reagents is necessary[81]. On the other hand the reaction of cyclones with vinyl ethers takes place more readily than with cyclopentadiene, giving higher yields of addition products under analogous conditions. Thus, ethyl vinyl ether, which did not give an addition product with cyclopentadiene, gave addition product (VIII) in 77% yield with acecyclone[76]. Analogous addition products were obtained with butyl vinyl and phenyl vinyl ethers.



where R = C_2H_5, C_4H_9, C_6H_5.

The reactions take place on heating the reagents in sealed tubes at 180–200°C for 10–15 h, and are accompanied by loss of the *endo*-carbonyl bridge and the alcohol. It has been shown[76] that allyl derivatives and vinyl bromide react with acecyclone with great difficulty.

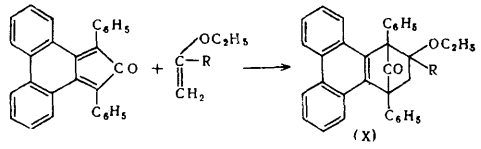
In the reaction with tetracyclone, carried out under analogous conditions[77] vinyl ethers were used: butyl vinyl, isopentyl vinyl, phenyl vinyl, and 1,2,3-trivinyloxypropane. These reactions take place by the equation:



In all the reactions 1,2,3,4-tetraphenylbenzene (IX) was obtained in good yield (74–86%).

Addition products of tetraphenylcyclone and acecyclone with ethyl 1-methylvinyl and ethyl 1-phenylvinyl ethers were obtained[78]. These condensations required more prolonged heating (up to 75 h).

Phencyclone reacts more readily than other cyclones with 1-substituted vinyl ethers[78], giving addition products with an *endo*-carbonyl bridge (X)

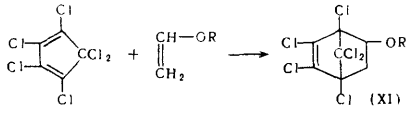


(X)

where R = CH_3, C_6H_5.

Of other dienes with electron-withdrawing substituents only the chloro-substituted dienes, mainly hexachloropentadiene, have been investigated in reactions with vinyl ethers and sulphides. Only one communication about the condensation of chloroprene with ethyl vinyl ether has been published[82], and in this the addition products could not be isolated from the reaction products.

Thanks to the presence of the electronegative chlorine atoms hexachlorocyclopentadiene has a diene system impoverished in electrons and therefore capable of showing electron-withdrawing properties. This can explain the much greater ease with which diene condensations proceed with nucleophilic dienophiles[62], including vinyl ethers. For example, with ethyl vinyl ether[83] hexachloropentadiene gave an addition product—1,2,3,4,7,7-hexachloro-5-ethoxybicyclo[2,2,1]hept-2-ene (XI)—in 36% yield on heating for 6 h at 80–90°C. Under analogous conditions an addition product is also obtained with isobutyl vinyl ether



(XI)

Analogous addition products were obtained with cyclohexenyl ethyl ether[84] on heating at 160°C for 8 h in a sealed tube.

By heating a mixture of phenyl vinyl ether and hexachlorocyclopentadiene at 120–130°C for 2 h, 1,2,3,4,7,7-hexachloro-5-phenoxybicyclo[2,2,1]hept-2-ene was obtained in 72% yield[69].

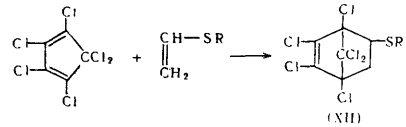
Addition products were also obtained with other aryl vinyl ethers, including naphth-2-yl vinyl and *p*-t-butylphenyl vinyl ethers[70].

Kalabina and coworkers[85] studied the reaction of vinyl ethers of *o*-, *m*-, and *p*-nitrophenols with hexachlorocyclopentadiene. These condensations proceed under more severe conditions in comparison with phenyl vinyl ether (in boiling xylene for 6.5 h) and give smaller yields of the addition products (11–15%).

The condensation of divinyl ether with hexachlorocyclopentadiene takes place[86] at 120°C and leads to 1,2,3,4,7,7-hexachlorobicyclo[2,2,1]hept-2-en-5-yl vinyl ether.

2,3-dihydrofuran reacts with hexachlorocyclopentadiene at an appreciable rate[62], much more rapidly than maleic anhydride.

A series of addition products have been obtained from vinyl sulphides. Thus ethyl vinyl sulphide[74], which did not give an addition product with cyclopentadiene at 110°C, gave one with hexachlorocyclopentadiene at room temperature after 36 days—1,2,3,4,7,7-hexachloro-5-ethylmercaptobicyclo[2,2,1]hept-2-ene in 71% yield. In another study[72] this reaction was carried out at 100–105°C (3.5 h) and then addition product (XII) was obtained in 83% yield:



(XII)

where R = C_2H_5, C_6H_5.

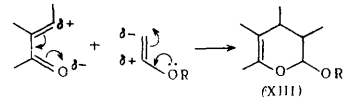
In the same work an addition product of hexachlorocyclopentadiene and phenyl vinyl sulphide was obtained (120°C, 3 h) in 71.5% yield.

In contrast to the electron-withdrawing substituents, electron-donating substituents of the diene system hinder the diene synthesis with vinyl ethers. Thus, furan and 2-methylfuran, which with maleic anhydride form addition products at room temperature in quantitative yields[86], did not give addition products with alkyl vinyl ethers even on heating at 280°C for many hours[87].

6. REACTIONS WITH HETERODIENES

A. Reactions with Oxygen Heterodienes

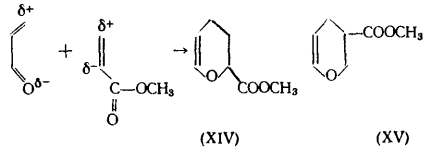
In 1950 Longley and Emerson[88] found that acrylaldehyde and other $\alpha\beta$-unsaturated aldehydes and ketones, on reacting as dienes, readily add vinyl ethers in the 1,4-position, to form the addition products (XIII) in accordance with the polarity of the reagents. For example, with acrylaldehyde they obtained 2-alkoxy-derivatives of dihydropyran:



(XIII)

The reactions were carried out by heating mixtures of the components in a bomb in the presence of a little hydroquinone at 135–200°C for 12–30 h. The yields of addition products were 50–85%.

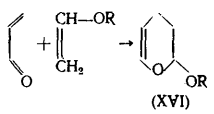
The diene systems of this type contain an electronegative oxygen atom, due to the polarisation of double bonds and imparting an electron-withdrawing character to the system as a whole. By this it was possible to explain the relative ease with which the condensation of such dienes with vinyl ethers is effected. These dienes also react with electron-withdrawing dienophiles, for example, with methyl acrylate[54]. As already stated above, here the reaction proceeds despite the polarity of the reagents and the addition product formed is 2-methoxycarbonyl-3,4-dihydro-2*H*-pyran (XIV) and not 3-methoxycarbonyl-3,4-dihydropyran (XV):



(XIV) (XV)

Hence although the presence of an oxygen atom also confers electron-withdrawing properties on the diene system, this system is capable of reacting also as electron-donating with dienes which exhibit strong electron-withdrawing properties.

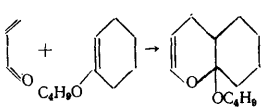
Diene condensations between $\alpha\beta$-unsaturated aldehydes or ketones and vinyl ethers have been studied for many examples[88-91]. In the work mentioned[88] it was shown that acrylaldehyde, on reacting with various alkyl vinyl ethers, forms 2-alkoxy-3,4-dihydro-2*H*-pyran (XVI) in up to 84% yield:



(XVI)

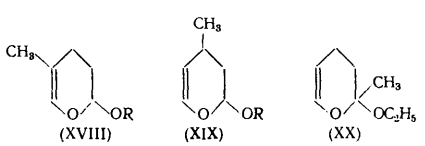
where R = CH_3, C_2H_5, C_4H_9, iso-C_4H_9.

In the reaction with butyl cyclohex-1-enyl ether the addition product obtained was 1-butoxy-2-oxabicyclo[4,4,0]dec-3-ene (XVII):



(XVII)

In the condensation of methylacrylaldehyde and crotonaldehyde with vinyl ethers 2-alkoxy-5-methyl- (XVIII) and 2-alkoxy-4-methyl- (XIX) 3,4-dihydro-2*H*-pyran are formed with yields of up to 87%:

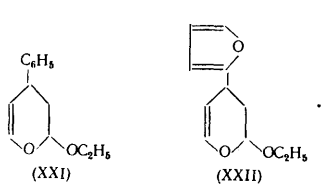


(XVIII) (XIX) (XX)

where R = CH_3, C_2H_5, C_4H_9, iso-C_4H_9.

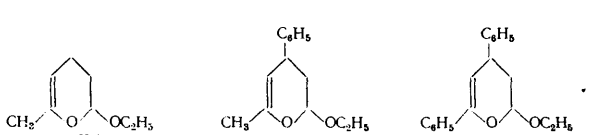
A low yield (25%) was obtained only in the condensation of methylacrylaldehyde with methyl vinyl ether. 2-Ethoxy-3,4-dihydro-2-methyl-2*H*-pyran (XX) was obtained in the condensation of acrylaldehyde with ethyl isopropenyl ether[88].

On condensation with ethyl vinyl ether, cinnamaldehyde and β(furfurylidene) acrylaldehyde give addition products (XXI) and (XXII) in 60–85% yield:



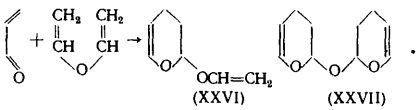
(XXI) (XXII)

On heating methyl vinyl ketone, benzalacetone, and benzalacetophenone with ethyl vinyl ether at 140–200°C for 13–16 h, derivatives of dihydropyran (XXIII), (XXIV), and (XXV) are obtained in yields of up to 75%:



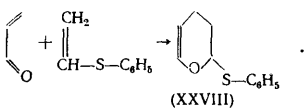
(XXIII) (XXIV) (XXV)

Independently of Longley and Emerson, Smith and coworkers[89] carried out a series of similar condensations, but under somewhat different conditions—they carried out the reaction at higher temperatures and for a shorter time, mainly by heating a mixture of the components without a solvent at 180°C for 1 h. The yields of addition products were as high. In addition, the authors studied the reaction of acrylaldehyde with divinyl ether and showed that here two addition products are formed—mono- (XXVI) and bis- (XXVII) addition products:



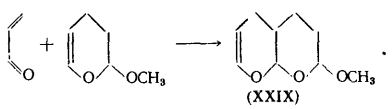
(XXVI) (XXVII)

In addition, addition products of acrylaldehyde with phenyl vinyl ether and phenyl vinyl sulphide were obtained. The latter gave addition product (XXVIII) in 77% yield:



(XXVIII)

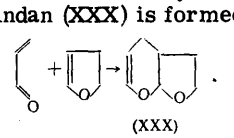
It was shown that the addition product of acrylaldehyde and methyl vinyl ether—3,4-dihydro-2-methoxy-2*H*-pyran—is capable of condensing with a second molecule of acrylaldehyde, giving (XXIX):



(XXIX)

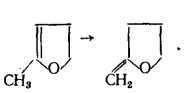
The structure of the addition products was shown by hydrolysis to the corresponding glutaraldehydes, and also by hydrogenation with subsequent hydrolysis of the tetrahydropyrans to 5-hydroxyvaleraldehyde and its derivatives.

Cyclic $\alpha\beta$-unsaturated ethers of the type of 4,5-dihydrofuran and 5,6-dihydropyran[92] under analogous conditions are readily condensed with $\alpha\beta$-unsaturated carbonyl compounds. Thus, on heating in an autoclave (140°C, 16 h) mixtures of 4,5-dihydrofuran and acrylaldehyde, 4,7,8,9-tetrahydro-1,7-dioxaindan (XXX) is formed:

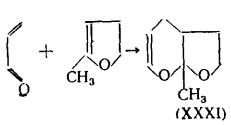


(XXX)

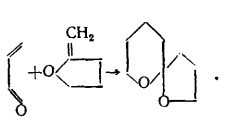
The condensation of 4,5-dihydro-2-methylfuran with acrylaldehyde under the same conditions is complicated by the isomerisation of the unsaturated ether into tetrahydro-2-methylenefuran:



This leads to the formation of two addition products, (XXXI) and (XXXII), in the ratio 7 : 3, with a total yield of 39%:



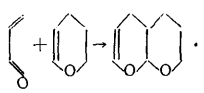
(XXXI)



(XXXII)

Addition product (XXXII) is formed with a yield of 60% in the condensation of acrylaldehyde with pure tetrahydro--2-methylenefuran. The structure of the addition products was shown by hydrogenation and subsequent hydrolysis with a yield of the compounds described.

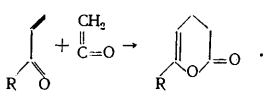
Dihydropyran was less active. On heating it with acrylaldehyde at 140°C for 15 h, Δ^2-octahydro-1,8-dioxanaphthalene (XXXIII) was obtained in only 15% yield:



(XXXIII)

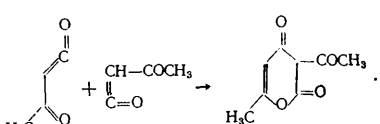
Hydrolysis of (XXXIII) led to 2-(3-hydroxypropyl)glutaraldehyde.

The condensation of a series of $\alpha\beta$-unsaturated carbonyl compounds with keten has been described[93]; these condensations proceed analogously to the reactions of alkyl vinyl ethers, leading to the δ-lactones (XXXIV):



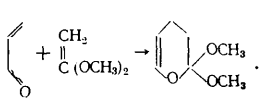
(XXXIV)

The dimerisation of diketen[94] proceeds by a diene synthesis scheme with formation of the addition product (XXXV):



(XXXV)

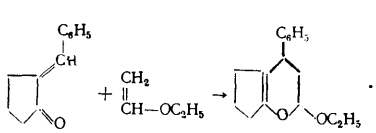
Condensations of a series of $\alpha\beta$-unsaturated aldehydes and ketones with keten dimethyl acetal [1,1-dimethoxyethylene] have been described[95]. With acrylaldehyde at 100°C, 5,6-dihydropyran-6-one dimethyl acetal (XXXVI) was obtained in 70% yield:



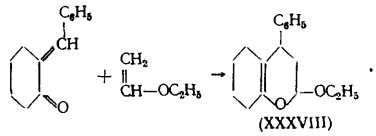
(XXXVI)

The condensation of cinnamaldehyde and benzalacetone with keten dimethyl acetal takes place at a higher temperature (150–200°C), giving the corresponding addition products with yields of 30–60%.

Heterodienes such as cyclic *o*-methyleneketones are also capable of the reactions of the diene synthesis with ethyl vinyl ether. It has been shown[96] that 2-benzylidenecyclopentanone and 2-benzylidenecyclohexanone with ethyl vinyl ether at 160–168°C form the corresponding addition products (XXXVII) and (XXXVIII) with yields of 38–52%:



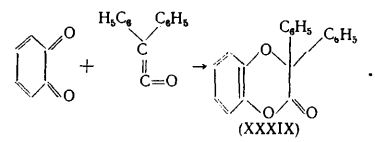
(XXXVII)



(XXXVIII)

The structure of these products was shown by conversion of (XXXVIII) into 4-phenylquinoline. 2-Arylideneindan-1,3-diones condense analogously with ethyl vinyl ether, forming addition products in yields of 43–49%.

Diphenylketen was found capable[97] of being condensed with *o*-benzoquinone, the diene system of which contains two oxygen atoms:

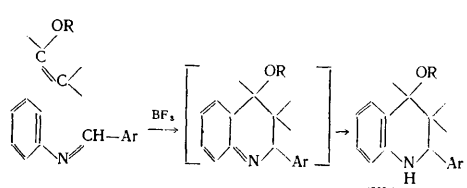


(XXXIX)

B. Reactions with Nitrogen Heterodienes

Almost the only known diene condensations of $\alpha\beta$-unsaturated ethers with nitrogen heterodienes are those with Schiff bases. In 1962 Povarov and Mikhailov [17,98] found that in the presence of boron trifluoride Schiff bases react readily with alkyl vinyl ethers to form addition products according to the diene synthesis scheme. It was shown subsequently that in the reaction with a Schiff base the dienophile can be ethoxyacetylene or keten [18], vinyl sulphide [18,99], the cyclic ethers 4,5-dihydro-2-methylfuran and dihydropyran [100,101], or cyclohexenyl ethyl ether [102]. A wide variety of Schiff bases with various substituents were used as dienes [101,103,104]. It was shown that the anils of non-aromatic aldehydes are also capable of participating in the reaction. For example, addition products were obtained with anils of cinnamaldehyde, citral, and cyclohexanone [101]. The anils of aliphatic aldehydes which are distinguished by a tendency to polymerisation are also capable of condensing with alkyl vinyl ethers at the moment of formation [105]. Apart from BF_3, $AlCl_3$ and $AlBr_3$ are also used as catalysts [19,101]. A diene synthesis between Schiff bases and alkyl vinyl ethers takes place in acetic acid which serves here as the catalyst [106]. The reactions were carried out in solvents such as ether, benzene, and ethyl acetate.

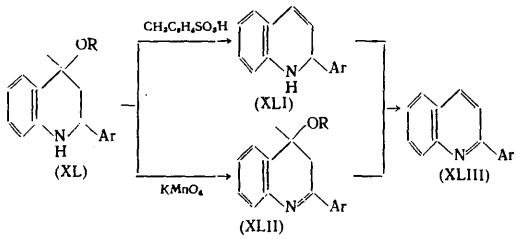
In the reaction of Schiff bases with alkyl vinyl ethers [17,107] derivatives of 4-alkoxy-2-aryl-1,2,3,4-tetrahydroquinoline (XL) are formed:



(XL)

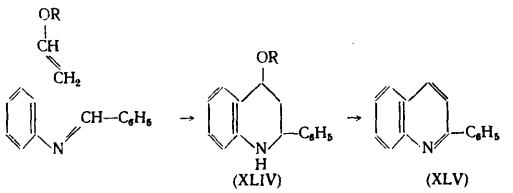
These compounds exhibit extremely weak basic properties; they do not give picrates and do not dissolve in dilute mineral acids. On heating with *p*-toluenesulphonic acid or under the action of oxidants they are converted into the corresponding derivatives of quinoline (XLIII). In the first instance alcohol is lost initially with the formation of 1,2-dihydroquinolines (XLI) and subsequently dehydrogenation takes place. In this part of the 1,2-dihydroquinoline molecule acts as an acceptor of hydrogen. Moreover, in

this example a polymer is formed as a result of the polymerisation of the 1,2-dihydroquinolines (XLI). The yields of quinolines here do not exceed 50%. Under the action of an oxidant ($KMnO_4$ in acetone), the hydrogen atoms in positions 1 and 2 are oxidised initially with the formation of 4-alkoxy-3,4-dihydroquinolines (XLII), then loss of an alcohol takes place readily, and the quinolines (XLIII) are formed with a yield of up to 90%:



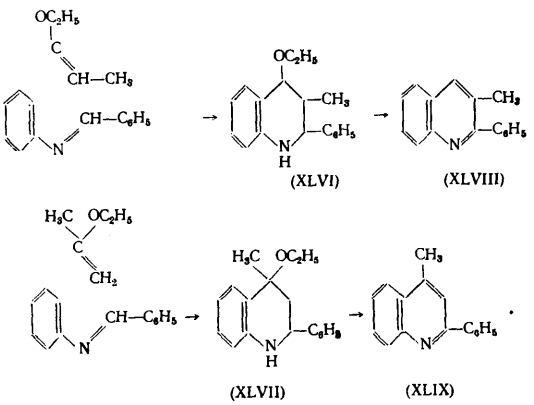
The partial loss of alcohol from addition products (XL) is observed during the reaction and during fractionation, which explains the formation in several instances of an appreciable polymeric residue and the drop in the yield of addition products.

In the condensation of benzylidineaniline with ethyl vinyl, isopropyl vinyl, and butyl vinyl ethers, 4-alkoxy-2-phenyl-1,2,3,4-tetrahydroquinolines (XLIV) were obtained with yields of up to 60%. The structure of the addition products was shown by conversion into 2-phenylquinolines (XLV):

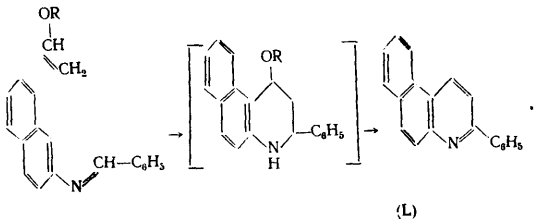


where R = C_2H_5, $CH(CH_3)_2$, C_4H_9.

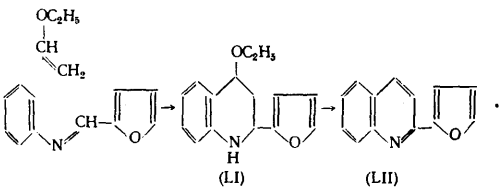
Ethyl prop-1-enyl and ethyl isopropenyl ethers gave respectively 3-methyl- (XLVI) and 4-methyl- (XLVII) 2-phenyltetrahydroquinolines, which were converted further into 3-methyl- (XLVIII) and 4-methyl- (XLIX) 2-phenylquinolines:



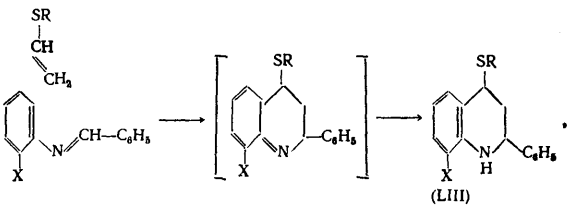
The yield of addition product (XLVII) was low because of the instability of the alkoxy-group at the tertiary carbon atom. The example of these condensations showed the structural directionality of the reaction. Addition products were obtained for alkyl vinyl ethers with a series of substituted benzylidene anils: salicylideneaniline, *o*-nitrobenzylideneaniline, benzylidene-*p*-bromoaniline, benzylidene-*p*-iodoaniline, benzylidene-*p*-anisidine, benzylidene-*p*-phenetidine, *N*-benzylideneanthranilic acid, etc. In several instances the intermediate tetrahydroquinolines (XL) were not isolated but the corresponding quinolines (XLIII) were obtained directly. For example, for benzylidene-2-naphthylamine 2-phenyl benzo[*f*]quinoline (L) is crystallised directly from the reaction mixture:



The condensation of furfurylideneaniline with ethyl vinyl ether led to 4-ethoxy-2-furyl-1,2,3,4-tetrahydroquinoline (LI) from which 2-furylquinoline (LII) was obtained in 36% yield:

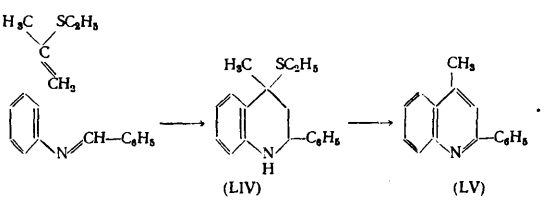


Alkyl vinyl sulphides react no less vigorously than alkyl vinyl ethers with Schiff bases [18,99]. Here the addition products formed are 4-alkylmercapto-1,2,3,4-tetrahydro-2-phenylquinolines (LIII) with yields of 40–60%:



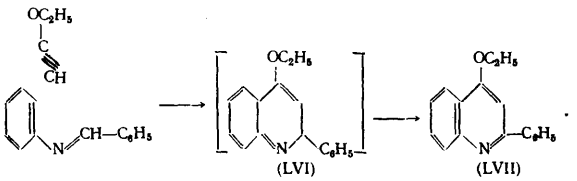
where R = C_2H_5, C_4H_9; X = H, CH_3, CO_2H.

The structure of the addition products was shown by converting them into the corresponding quinolines, which was brought about by heating with *p*-toluenesulphonic acid. This results in the loss of mercaptan and hydrogen. The structural directionality of the reaction was shown by the example of the condensation of benzylideneaniline with ethyl isopropenyl sulphide. The 4-ethylmercapto-1,2,3,4-tetrahydro-4-methyl-2-phenylquinolines (LIV) thus obtained gave, under the action of *p*-toluenesulphonic acid, 4-methyl-2-phenylquinoline (LV):



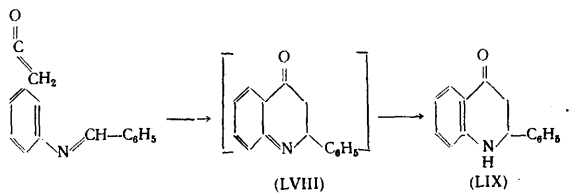
It was shown that the weaker the basicity of the Schiff bases the more readily they react with alkyl vinyl sulphides. Thus the condensation of benzylidene-*p*-anisidine and benzylidene-*p*-phenetidine, the basic properties of which are higher than those of benzylideneaniline, proceeded with difficulty. The only addition products isolated were 6-methoxy- and 6-ethoxy-2-phenylquinolines with yields of 6.6 and 34.7% respectively.

The reaction of ethoxyacetylene with benzylideneaniline[18] leads to 4-ethoxy-2-phenylquinoline (LVII). Addition product (LVI), which is produced initially in accordance with the diene synthesis scheme, is unstable and, on losing hydrogen, is converted into the stable compound (LVII):



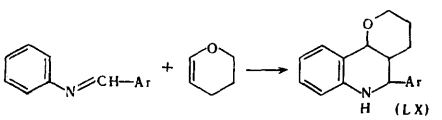
(LVI) (LVII)

In the reaction of benzylideneaniline with keten[18] the addition product (LVIII) which is formed initially is isomerised into 2,3-dihydro-2-phenylquinol-4-one (LIX):



(LVIII) (LIX)

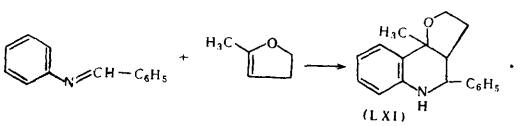
Cyclic ethers, such as dihydropyran and dihydrosylvan, are also capable of being condensed with Schiff bases. Dihydropyran[100] gave 2-aryl-3,4:3′,2′-tetrahydropyrano-1,2,3,4-tetrahydroquinolines (LX):



(LX)

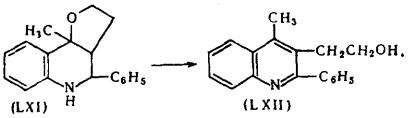
where Ar = C_6H_5, 

An especially active dienophile in relation to Schiff bases is dihydrosylvan, from which a large number of addition products was obtained, the yields reaching 70–80% in many instances. Usually the addition products are stable crystalline substances. Thus with benzylideneaniline[100], 4-methyl-2-phenyl-3,4:3′,2′-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (LXI) was obtained in 81.3% yield:



(LXI)

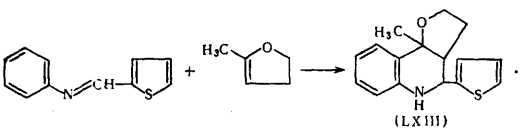
By the action of $KMnO_4$ in acetone[108] on addition product (LXI) the hydrogen atoms in positions 1 and 2 are readily oxidised and the furan ring is opened to form 3-(2-hydroxyethyl)-4-methyl-2-phenylquinoline (LXII):



(LXI) (LXII)

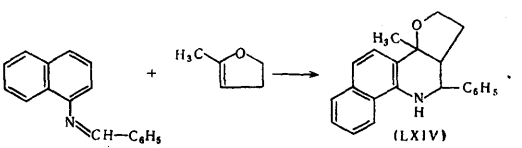
Addition products of dihydrosylvan with various substituted Schiff bases have been obtained[100,101,103,104].

4-Methyl-2-(2-thienyl)-3,4:3′,2′-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (LXIII) was obtained by the condensation of dihydrosylvan with thienylideneaniline[100]:



(LXIII)

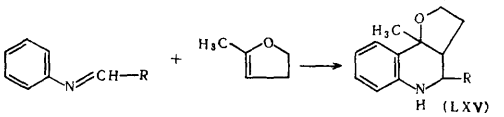
With benzylidene-1-naphthylamine[100] addition product (LXIV) was obtained:



(LXIV)

The reactions of unsaturated ethers with Schiff bases proceed stereospecifically with the formation of a single addition product. Only in certain instances were low-melting isomers isolated in an insignificant amount, their infrared spectra being identical with those of the high-melting addition products[104]. The ratio of the isomers depends on the reaction temperature. At an elevated temperature the amount of the low-melting isomer can become predominant as was shown by the example of the reaction of benzylidene-*p*-methoxycarbonylaniline with dihydrosylvan[19]

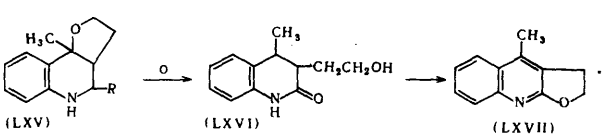
The anils of cinnamaldehyde and citral gave addition products (LXV) containing a vinyl group in position 2:[101]



(LXV)

where R = $-CH=CH-C_6H_5$; $-CH=C(CH_3)CH_2CH_2CH=C(CH_3)_2$.

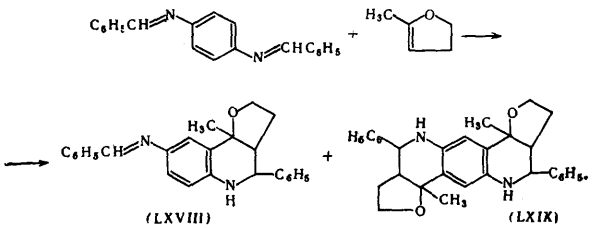
In the oxidation of addition products (LXV) with $KMnO_4$ in both instances 3-(2-hydroxyethyl)-4-methylquinol-2-one (LXVI) was obtained[108], which is readily cyclised under the action of polyphosphoric acid into 4-methyl-2,3:2′,3′-dihydrofuranoquinoline (LXVII):



(LXV) (LXVI) (LXVII)

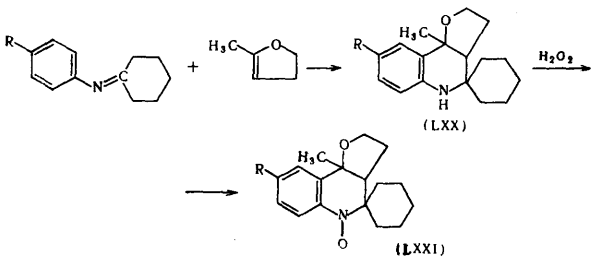
These conversions showed the structure of addition products (LXV), which was also confirmed by infrared spectra.

In the reaction of dihydrosylvan with bis-*N*-benzylidene-*p*-phenylenediamine [19] mono- (LXVIII) or bis- (LXIX) addition products can be obtained, depending on the ratio of the reagents:



(LXVIII) (LXIX)

The reaction of dihydrosylvan with cyclohexanone anils [101,109,110] leads to addition products (LXX), which contain a spirocyclohexyl substituent in position 2. Their oxidation with hydrogen peroxide in the presence of sodium tungstate gave [109-111] stable nitroxide radicals (LXXI):

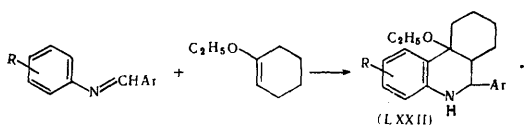


(LXX) (LXXI)

where R = H, OCH_3.

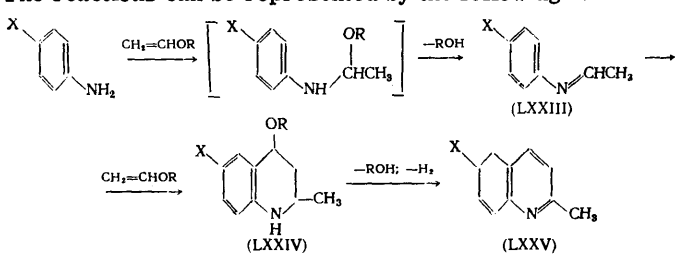
The reaction of cyclohexylidene-1-naphthylamine and cyclohexylidene-2-naphthylamine with dihydrosylvan [109] was used to synthesise 7,8- and 5,6-benzo-derivatives of quinoline of type (LXX), from which stable nitroxide radicals were also obtained.

The reactions of Schiff bases with cyclohex-1-enyl ethyl ether [102] is of special importance since here hydrogenated 9-arylphenanthridines (LXII) are formed:



(LXXII)

Povarov and Mikhailov [105] showed that the anils of aliphatic aldehydes are capable of diene condensations with alkyl vinyl ethers. The reaction conditions were such that the anils of acetaldehyde (LXXIII) reacted with the alkyl vinyl ethers at the moment of formation. This occurred in the reaction of aromatic amines with alkyl vinyl ethers in the presence of boron trifluoride. During this, 4-alkoxy-1,2,3,4-tetrahydroquinaldines (LXXIV) were formed, which under the action of *p*-toluenesulphonic acid were converted into the corresponding quinaldines (LXXV). The reactions can be represented by the following scheme:

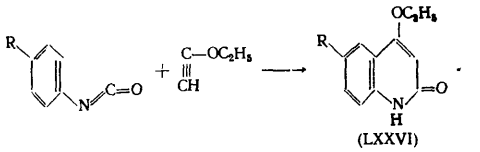


(LXXIII) (LXXIV) (LXXV)

where X = H, OCH_3, Br; R = C_2H_5, C_4H_9.

The reaction usually starts at 30–35°C and subsequently proceeds with liberation of heat. The yields of tetrahydroquinaldines (LXXIV) are 30–50%. In the condensation of 2-naphthylamine with butyl vinyl ether, 5,6-benzoquinaldine was obtained directly.

On other reactions of nitrogen heterodienes with unsaturated ethers the literature contains only a few examples of the condensation of ethoxyacetylene with arylisocyanates [112,113], as a result of which 4-ethoxyquinol-2-ones (LXXVI) were obtained:



(LXXVI)

This reaction has been carried out with phenyl, *p*-tolyl, 1-naphthyl, and *p*-nitrophenyl isocyanates. After 6 months at room temperature an addition product of phenyl isocyanate with ethoxyacetylene was obtained in 42% yield. Resinification occurred at high temperatures.

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REARRANGEMENT OF ACETYLENIC COMPOUNDS WITH PARTICIPATION OF THE π-ELECTRONS OF THE TRIPLE BOND

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INTRODUCTION

After the discovery of the isomerisation of acetylenic hydrocarbons, the rearrangement of acetylenic compounds containing the most diverse functional groups became the subject of many investigations. It was found that acetylenic, vinylacetylenic, and diacetylenic compounds which contain a hydroxyl group, halogens, sulphur, nitrogen, phosphorus, etc. smoothly undergo various rearrangements with the formation of isomeric compounds. Most of these rearrangements are unique, and often the only method of making previously inaccessible new classes of unsaturated alcohols, aldehydes, ketones, and other compounds.

A review of rearrangements of acetylenic compounds has not appeared in the literature, with the exception of Jasiobedzki's article [1] dealing only with the acetylene–allene rearrangement.

In the present article we have tried to collect, and as far as possible, systematise the very interesting and abundant material relating to this subject which has now accumulated.

I. PROTOTROPIC REARRANGEMENT OF ACETYLENIC HYDROCARBONS

During the synthesis of acetylenic hydrocarbons from dihalogenoalkyls Favorskii [2] found that instead of the expected monosubstituted acetylenes disubstituted compounds are obtained. He concluded that under the conditions of the experiment isomerisation of the triple bond along the chain occurred. Subsequently he and his coworkers [3-8] found that various alk-1-ynes isomerise into the

corresponding alk-2-ynes when heated with alcoholic potassium hydroxide solution to 170°C:

$$R{-}CH_2C{\equiv}CH \rightarrow R{-}C{\equiv}C{-}CH_3.$$

On heating disubstituted acetylenes with metallic sodium the reverse process takes place, that is, they are converted into monosubstituted acetylenes[9-15]:

$$R{-}C{\equiv}C{-}CH_3 \rightarrow R{-}CH_2C{\equiv}CH.$$

Hence Favorskii discovered the very interesting reversible isomerisation of acetylenic hydrocarbons [alkynes]. Detailed study of the mechanism of this reaction led the authors to conclude that it proceeds through allenic compounds according to the scheme:

$$R{-}CH_2C{\equiv}CH \rightarrow R{-}CH{=}C{=}CH_2 \rightarrow R{-}C{\equiv}C{-}CH_3.$$

Direct confirmation of this is provided by the fact that under analogous conditions[2,10,16-19] allenic hydrocarbons are isomerised into acetylenes.

Subsequently an analogous rearrangement was observed also in the dehydrohalogenation of polyhalogeno-compounds by sodium amide[20-23].

Isomeric conversions of acetylenic hydrocarbons were widely studied[24-47]. Various examples showed that the triple bond can migrate to either the middle[24-42] or the end[42-47] of the chain.

It must be noted that in dehydrohalogenation by solid or molten alkali without a solvent the specified isomerisation proceeds very weakly or is generally not observed[16].

It has been found that in several instances dehydrohalogenation of polyhalogeno-compounds often leads, not to the expected non-conjugated alkadiynes, but to conjugated alkadiynes[16,48-52]:

$$CH_2BrCHBrCH_2CH_2CHBrCH_2Br \rightarrow \begin{cases} HC{\equiv}C{-}CH_2CH_2C{\equiv}CH \\ H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \end{cases}.$$

Recently a series of authors[53] have also studied the isomeric conversions of various alkadiynes.

Thus it has been shown that when non-conjugated diacetylenes are heated with alkaline agents (potassium hydroxide, sodium amide, etc.) they are isomerised into conjugated diacetylenes[53-55]. When the reaction is carried out in the presence of potassium t-butoxide, both vinylacetylenic and diacetylenic hydrocarbons are converted into conjugated polyenes and polyenynes respectively[56,57]:

$$\begin{array}{ll} RC{\equiv}CCH_2CH_2C{\equiv}C{-}R' & R{-}C{\equiv}CCH_2CH_2C{\equiv}C{-}R' \\ \downarrow & \downarrow \\ R{-}CH{=}CHCH_2C{\equiv}C{-}R' & R{-}CH{=}C{=}CHCH_2C{\equiv}C{-}R' \\ \downarrow & \downarrow \\ R{-}(CH{=}CH)_3R' & R{-}(CH{=}CH)_2C{\equiv}C{-}R' \end{array}.$$

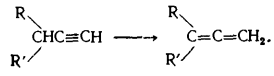
In the presence of potassium t-butoxide various cyclic polyacetylenes are converted into conjugated enynes[58-62] or dienes[63].

As well as the catalysts mentioned, metal oxides, fluorides, and other catalysts have been used for the rearrangement of acetylenic hydrocarbons[64-80]. The isomerisation of acetylenic[7,8,81,82] or vinylacetylenic[83] hydrocarbons was also observed during their alkylation by methyl iodide in the presence of metallic sodium.

Usually the isomerisation of acetylenic hydrocarbons takes place at 160–250°C. Isomerisation does not occur at lower temperatures[34,84,85]. It has been shown experimentally[86] that isomerisation proceeds readily when in monosubstituted acetylenic compounds there is a primary radical at the acetylenic carbon atom:

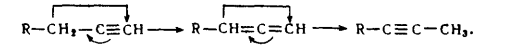
$$R{-}CH_2C{\equiv}CH \rightarrow R{-}C{\equiv}C{-}CH_3.$$

With a secondary substituent at the carbon atom the isomerisation proceeds only to the allene compound:

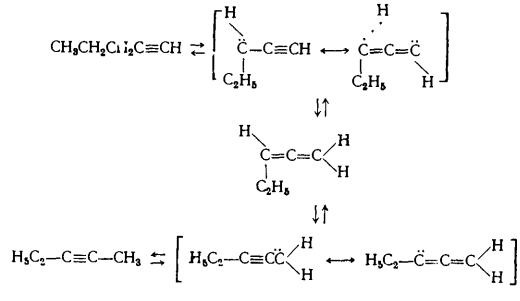


When the substituent in these compounds is a tertiary radical, isomerisation generally does not occur.

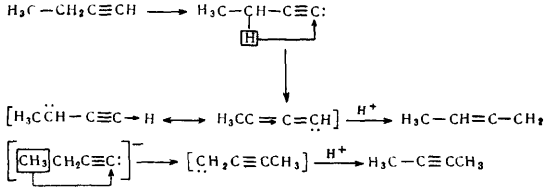
After detailed study of the reaction of mutual conversions of acetylenic compounds, Favorskii[86] concluded that the isomerisation of acetylenes in alcoholic solutions takes place not by addition and loss of the alcohol, as he thought earlier[2], but simply by jumping over of the β hydrogen atom with simultaneous migration of a multiple bond:



In the opinion of Jacobs and coworkers[75] and of other authors[87,88] under the action of alkali deprotonation of one of the labile α hydrogen atoms of the acetylenic or allenic compound takes place. Subsequently the intermediate carbonium ion which is formed rearranges according to the scheme:



Müller[89] suggests that in the isomerisation of acetylenic compounds the proton is detached not from the methylene but from the methine [presumably methylidyne (Ed. of Translation)] group; the anion formed undergoes cationotropic or prototropic rearrangement according to the scheme:

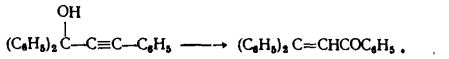


II. ANIONOTROPIC REARRANGEMENT OF ACETYLENIC ALCOHOLS

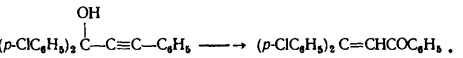
1. Rearrangement of Acetylenic Alcohols into $\alpha\beta$-Unsaturated Ketones. The Meyer–Schuster Rearrangement

In studying the reaction of acetyl chloride with phenylethynyldiphenylcarbinol [1,1,3-triphenylprop-2-yn-1-ol],

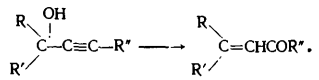
Meyer and Schuster[90] isolated phenylbenzalacetophenone [β-phenylchalcone]:



The authors found that this ketone was the only product when acetyl chloride was replaced by thionyl chloride, hydrogen chloride, acetic anhydride, or sulphuric acid. They showed, by the example of phenylethynyldi-(*p*-chlorophenyl)carbinol [1,1-di-(*p*-chlorophenyl)-3-phenylprop-2-yn-1-ol] that in the above rearrangement it is the hydroxyl group, not the aromatic radical, that migrates:

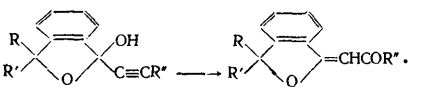


Subsequently various acetylenic alcohols with aliphatic, alicyclic, and aromatic substituents were subjected to rearrangements of this type in the presence of various acid agents[91-106]:

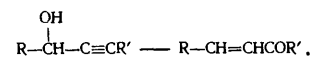


To obtain the best yield it was necessary to carry out the reaction in solvents; often dioxan, acetone, alcohols, and esters of organic acids were used. Acids (sulphuric, formic, sulphonic, etc.) were used as catalysts.

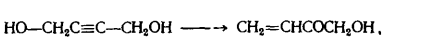
Recently Venus-Danilova and her coworkers have shown that ethynyl derivatives of hydroxyphthaleins undergo the Meyer–Schuster reaction[107,108]:



It has been shown that the rearrangement of secondary acetylenic alcohols proceeds analogously[104]:



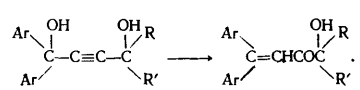
With acetylenic 1,4-glycols the rearrangement leads to the production of α-hydroxy-αβ-unsaturated ketones[109-111]:



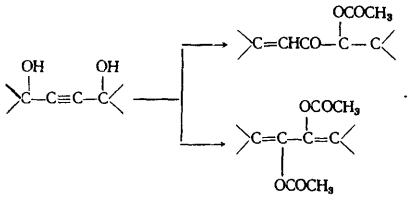
When the reaction is carried out in alcoholic solutions β-alkoxy-α-hydroxyketones or furanidones are formed[110-117].

In the rearrangement of primary-tertiary acetylenic glycols[118,119] under Meyer–Schuster conditions the hydroxyl group which migrates is that connected with the tertiary carbon atom.

In acetylenic glycols with aromatic and aliphatic substituents, on rearrangement it is the hydroxyl group at the carbon connected with the aromatic substituent that migrates[118-122]:

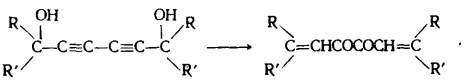


With alicyclic and aromatic symmetrical glycols both hydroxyls migrate, with the formation of acetates of keto-alcohols or diacetates of enols[118,123,124]:

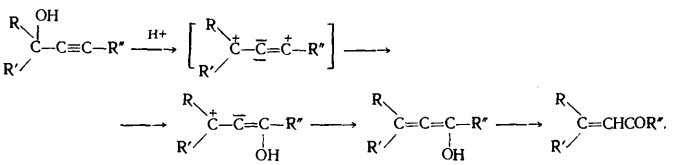


In all instances when the reaction proceeds in the presence of acetyl chloride acetoxy-derivatives of the keto-alcohols produced are obtained.

It was shown recently that on heating diacetylenic glycols in methanol solution in the presence of mercury sulphate they undergo rearrangement with the formation of unsaturated α-diketones[125]:



Dornow and Ische[126] suggest that the Meyer–Schuster rearrangement proceeds by a carbonium ion mechanism with formation of an intermediate vinyl alcohol and its subsequent isomerisation into a vinyl ketone:

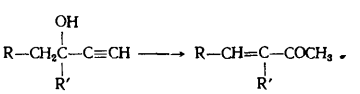


2. Rearrangement of Acetylenic Alcohols into αβ-Unsaturated Aldehydes and Ketones

The rearrangement of acetylenic alcohols with an active acetylenic hydrogen was first studied by Rupe and coworkers. They showed that when acetylenic alcohols react with formic acid they are rearranged into αβ-unsaturated aldehydes[127-135]:



Subsequent studies[136-138] did not confirm the results of Rupe and coworkers. The authors cited reported that αβ-unsaturated ketones, not aldehydes, are obtained in the rearrangement of acetylenic alcohols with active acetylenic hydrogen:

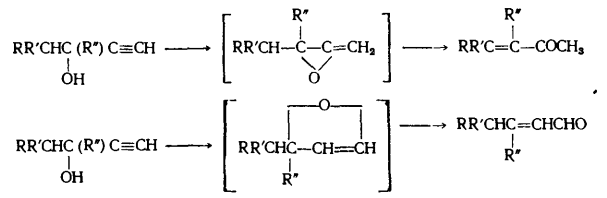


It must be noted that in the work there are no convincing data on the absence of the isomeric aldehydes.

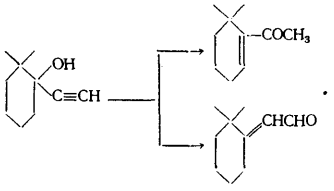
In later communications Rupe and coworkers also mention that ketones are also formed as well as aldehydes[131,134,139].

To explain the chemistry of the formation of aldehydes and ketones, the authors propose a mechanism for the

rearrangement with the intermediate formation of oxidic compounds [134]:

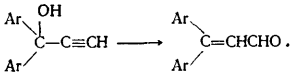


Chanley [140] showed convincingly that in the rearrangement of 1-ethynylcyclohexan-1-ol and its derivatives, in addition to ketones the corresponding $\alpha\beta$-unsaturated aldehydes are formed, in particular 1-ethynylcyclohexan-1-ol gives 50% of the expected ketone and 0.8% aldehyde, and 1-ethynyl-2,2-dimethylcyclohexan-1-ol gives 56% of the ketone and 6% of the aldehyde:



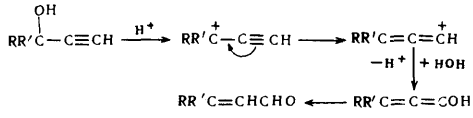
Despite this, in several papers the authors state that in the rearrangement of acetylenic alcohols with aliphatic [141-146], alicyclic [103,141,147-152], and aromatic [153] substituents only the $\alpha\beta$-unsaturated ketones are obtained. Other papers give results showing that in the isomerisation of a series of aliphatic [154-157] and alicyclic [158,159] acetylenic alcohols in addition to the ketones the corresponding $\alpha\beta$-unsaturated aldehydes are isolated.

In contrast to the above results the rearrangement of aromatic acetylenic alcohols with an active acetylenic hydrogen leads to the formation mainly of the expected aldehydes [104 160-169]:

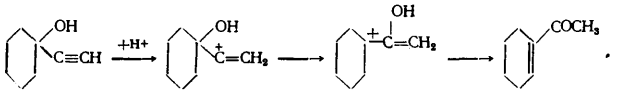


According to Bergmann [154], in the catalytic isomerisation of ethynyldimethylmethanol [2-methylbut-3-yn-2-ol] in the vapour phase β-methylcrotonaldehyde is formed in 30% yield. Other results have been published about the rearrangement of various acetylenic alcohols into aldehydes or ketones in the presence of various catalytic agents [170-176].

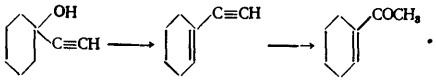
Hennion and coworkers [144] represent the mechanism of the rearrangement of ethynylcarbinols as an allyl rearrangement:



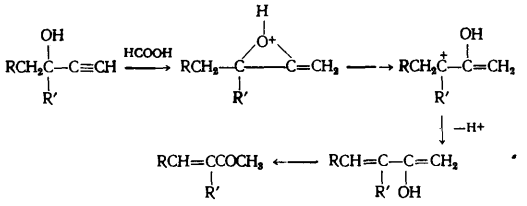
Newman [146,155] suggests that the rearrangement of ethynylcarbinols into $\alpha\beta$-unsaturated ketones proceeds by a carbocation mechanism:



Others think [138,144,177] that under the reaction conditions acetylenic alcohols are dehydrated into enynes and their subsequent hydration leads to the formation of ketones:



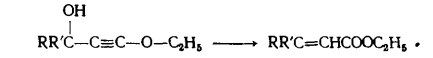
Cram and Hammond [178] explain the formation of $\alpha\beta$-unsaturated ketones by the following scheme:



It is evident that the mechanism of the formation of aldehydes and ketones from acetylenic alcohols has not been established and additional studies are needed.

3. Rearrangement of Alkoxyacetylenic Alcohols into the Esters of $\alpha\beta$-Unsaturated Acids

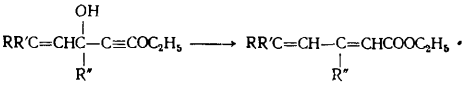
In the presence of sulphuric or hydrochloric acids alkoxyacetylenic alcohols undergo anionotropic rearrangement with the formation of the esters of $\alpha\beta$-unsaturated acids [179-182]:



Arens and coworkers [183] showed that alkoxyacetylenic alcohols are also rearranged in the presence of weakly basic amines, particularly in the presence of nitroaniline.

Heterocyclic [184], aldehydo- [185], and keto- [186] alkoxyacetylenic alcohols undergo this reaction.

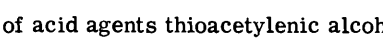
Esters of dienic acids are obtained in the rearrangement of vinyl(alkoxy)acetylenic alcohols [179,180,187]:



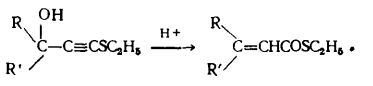
Alcohols in which the double bond is in the $\beta\gamma$-position or further removed undergo rearrangement in an analogous manner [187,189].

This reaction has been used for the preparation of perfumes [180,190], steroids [191-196], and terpenes [197]. Other studies of the rearrangement of various alkoxyacetylenic alcohols have appeared [198,199].

It has been shown that in the reaction of carbonyl-containing compounds with ethoxyacetylene in the presence of BF_3, esters of $\alpha\beta$-unsaturated acids are formed [200]:

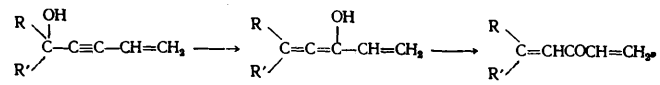


In the presence of acid agents thioacetylenic alcohols are also rearranged in an analogous manner [201,202]:



4. Rearrangement of Vinylacetylenic and Divinylacetylenic Alcohols

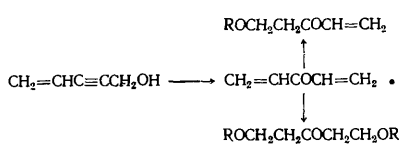
Nazarov and coworkers have shown that in acetone solution in the presence of mercury sulphate vinylacetylenic alcohols are isomerised into divinylketones by the following scheme[203,204]:



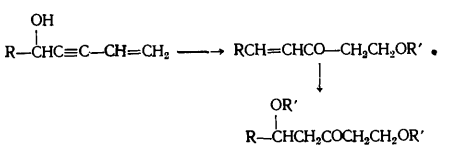
This reaction was carried out with a yield of ketone up to 40% for dimethyl(vinylethynyl)methanol [2-methylhex-5-en-3-yn-2-ol] alone. On increasing the molecular weight of the tertiary alcohol the reaction proceeds with difficulty and the yields of the divinyl ketones do not exceed 5% owing to side-reactions, particularly the dehydration and cyclodehydration of the alcohol.

It was found later that the isomerisation of vinylacetylenic alcohols takes place exceptionally readily in a solution of alcohols capable of adding to divinyl ketones. BF_3.HgO and mercury sulphate are catalysts for isomerisation[204,205]. The ease of isomerisation under these conditions (especially in methanol) is explained by the fact that the divinyl ketones formed are converted by addition of the alcohols into β-alkoxyketones and leave the sphere of reaction.

The isomerisation of the primary vinylethynylmethanol under these conditions leads to the formation of a divinyl ketone. Under the conditions of the experiment one or two methanol molecules add to the latter to form 1-methoxypent-4-en-3-one and 1,5-dimethoxypentan-3-one[206]:

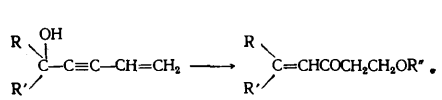


In solution in alcohols in the presence of mercury salts secondary vinylethynylmethanols are isomerised into divinyl ketones, which readily add one molecule of the alcohol at the unsubstituted vinyl group to form unsaturated alkoxy-ketones[207]:

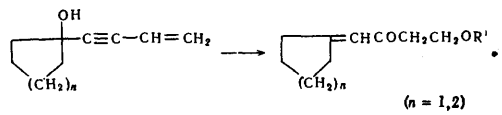


Under the influence of mercury salts a second alcohol molecule can be added to a β-alkoxyvinyl ketone to form dialkoxy-ketones.

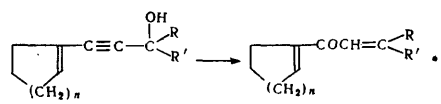
A still greater number of stages is observed in the addition of alcohols to ββ-dialkyldivinyl ketones [bis-(2-alkylvinyl)ketones]. Thus in the isomerisation of tertiary vinylacetylenic alcohols usually only one molecule of alcohol can be added to the divinyl ketones formed at the unsubstituted vinyl group and during this the corresponding unsaturated β-alkoxy-ketones are mainly formed[204,205,208,209]:



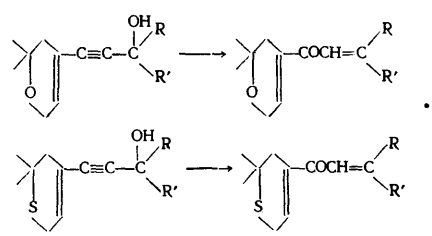
It has been shown that alicyclic vinylacetylenic alcohols are also rearranged with the formation of a mixture of the corresponding divinyl and β-alkoxy-ketones[210,211]:



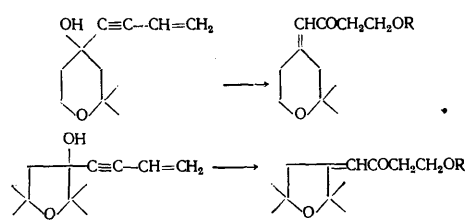
The isomerisation of Δ′-cyclohexenylethynylmethanols[212] and also of Δ′-cyclopentenylethynylmethanols[213] leads to the formation of divinyl ketones:



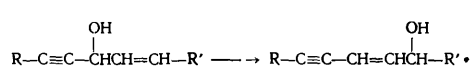
The isomerisation of vinylacetylenic alcohols which contain a vinyl group in the heterocyclic ring undergo isomerisation in an analogous manner[214-216]:



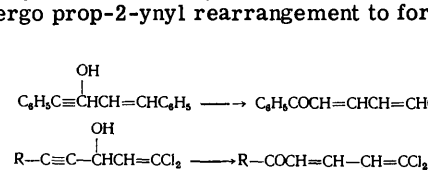
Many results on the rearrangement of vinylacetylenic alcohols containing various substituents have been published[217-226]. It has been found that 4-(vinylethynyl)tetrahydropyran-4-ols[226,227] and also vinylacetylenic furanols[228] undergo isomerisation with the formation of the expected ketones:



It is interesting to note that vinylacetylenic alcohols (A), depending on the nature of the substituent, undergo either allyl or prop-2-ynyl rearrangement. Thus the carbinols (A) undergo the allyl rearrangement[229-248]:

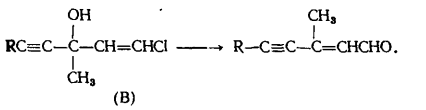


When R and R′ are electron-acceptor atoms or groups, particularly chlorine[102] or phenyl radicals[249], these alcohols undergo prop-2-ynyl rearrangement to form divinyl ketones:



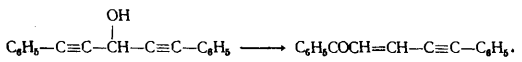
The prop-2-ynyl rearrangement is also observed when in the alcohols (A) R = C_6H_5 and R′ is a methyl[249] group or

hydrogen[169]. It is curious that the monochlorovinylacetylenic alcohols (B) undergo an allyl rearrangement under analogous conditions[250]:



(B)

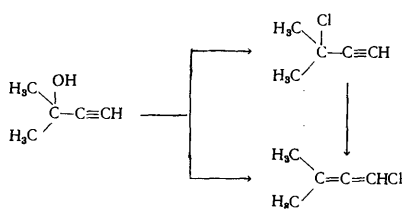
It has been found that diacetylenic methanols also rearrange in a similar manner[104]:



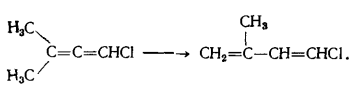
III. ACETYLENE–ALLENE REARRANGEMENT

1. Rearrangement of α-Halogenoacetylenes

Favorskii and Favorskaya found that reaction of dimethylethynylmethanol with hydrogen chloride in the presence of copper(I) chloride and ammonium chloride gives, in addition to the expected chloroalkyne, a derivative of allyl chloride[251]:



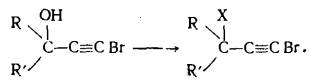
It was shown later that under the specified conditions chloroacetylene is actually rearranged into chloroallene[252]. On prolonged standing over ammonium chloride and copper(I) chloride, the latter is subjected to allene–diene rearrangement with the formation of the diene chloride[252]:



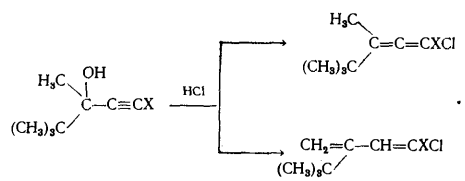
In studying the reaction of hydrogen chloride with dimethylethynylmethanol Hennion and coworkers[253] showed that when the reaction is carried out in the presence of calcium chloride, chloroacetylene is obtained in good yield. However, when the reaction is carried out in the presence of copper(I) chloride and ammonium chloride the main reaction product is allenyl chloride. An analogous picture is also observed with other acetylenic alcohols[143,254,255]. According to the results of Favorskaya[256–258] and others[143,259–261] this reaction proceeds similarly with hydrogen bromide. Campbell and coworkers[262] showed that in the reaction of hydrogen chloride with ethylethynylmethylmethanol the expected isomeric chloro-compounds are obtained. Favorskaya[263] showed that when this reaction is carried out in the presence of copper(I) chloride and ammonium chloride the chloroalkyne which is formed slowly rearranges into both the allenyl chloride [chloroalka-1,2-diene] and the diene chloride. When the reaction is carried out without catalysts[143] a chloroalkyne is mainly obtained.

Isomerisation of 3-chloro-3-ethylpent-1-yne proceeds even more slowly; a chloroalka-αβ-diene is still obtained but does not rearrange into the diene [chloride][264].

In the hydrochlorination of t-butylethynylmethylmethanol [3,4,4-trimethylpent-1-yn-3-ol] the sole product of the reaction is a chloroalka-1,2-dien[265]. Dialkyl(bromoethynyl)methanols react with hydrogen halides to form the corresponding halogenoalkynes[266]:



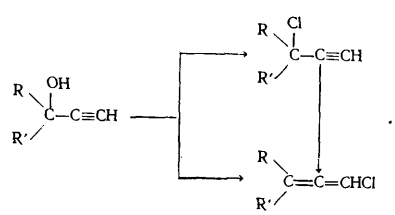
It was found also that t-butyl(halogenoethynyl)methylmethanols react with hydrogen chloride to give chloroalka-1,2-dienes[267] but the corresponding bromo-alcohols give mainly the bromoalka-1,3-dienes:



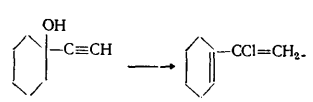
Dialkylethynylcarbinols react with hydrogen chloride[268,269] or phosphorus(III) chloride[270] to form chloroacetylene; however, according to the results of other authors[92], the action of hydrogen bromide on this alcohol gives, in addition to bromoalkynes, halogen derivatives of allene.

All attempts to carry out this reaction with other dialkylethynylcarbinols were unsuccessful[271,272]. The acetylene–allene rearrangement was also observed in the reaction of secondary acetylenic alcohols with hydrogen halides[255,273].

The reaction of aliphatic ethynylcarbinols with thionyl chloride[273,274] or phosphorus(V) chloride[275] in ethereal solution leads to the formation of two isomeric chlorides:

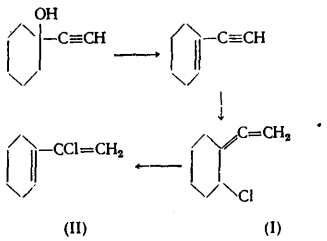


It should be noted that when a bromoallene derivative is formed in the reaction of tertiary acetylenic alcohols with $[(C_6H_5O)_3PBr_2]$, secondary and primary acetylenic alcohols form only bromoalkynes[261]. Jones and coworkers[276] found that thionyl chloride reacts with ethynylcyclohexanol in the presence of pyridine to give 1-chlorovinylhexene:



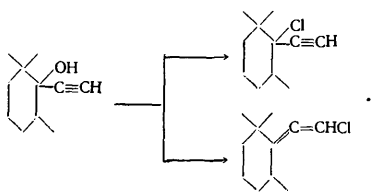
We think that a diene chloride could be obtained by the dehydration of an acetylenic alcohol followed by the addition of hydrogen chloride to the enyne formed in the 1,4 position to give an allenic chloride (I). The latter isomerises

under the conditions of the experiment into the diene chloride (II):



The formation of chlorides in the work of Bergmann and others[275] can be explained similarly.

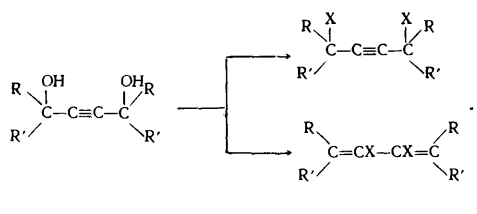
In the reaction of ethynylcyclohexanol and other alicyclic ethynylcarbinols with thionyl chloride in the presence of pyridine in various solvents both acetylenic and allenic chlorides are formed[255,272]:



Acetylene–allene rearrangement was also observed in the reaction of thionyl chloride with aromatic acetylenic alcohols[278]. It was shown that when prop-2-ynyl halides are heated in the presence of copper salts they are rearranged into halogenoalka-$\alpha\beta$-dienes[279]; during this, partial isomerisation of the halogenoalka-$\alpha\beta$-dienes was also noted.

Other information on the rearrangement of halogenoacetylenes into halogenoalka-$\alpha\beta$-dienes is available[280-285].

The reaction of acetylenic glycols with hydrogen halides leads to the formation of dichlorodienes (III)[286-302] by the scheme:



(III)

It was found that in the action of hydrogen halides on acetylenic 1,4-glycols hydroxyl is replaced by halogen and acetylenic dihalogeno-derivatives are obtained. Under the reaction conditions the latter undergo isomerisation into dihalogeno-derivatives of dienes.

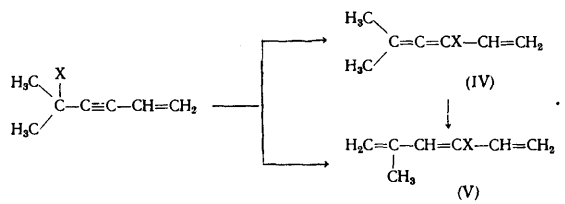
According to Johnson[109] 1,4-dibromo- or 1,4-di-iodobut-2-ynes are converted on standing into 2,3-dihalogenobutadienes:

$$XCH_2C{\equiv}CCH_2X \longrightarrow CH_2{=}CX{-}CX{=}CH_2.$$

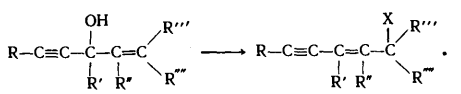
1,4-Dichlorobutynes rearrange similarly in the presence of copper(I) chloride and ammonium chloride[303].

Nazarov and coworkers[304] showed that on shaking chlorodimethyl(vinylethynyl)methane with copper(I) chloride and ammonium chloride at room temperature it undergoes rearrangement with the formation of allenic (IV) and trienic (V) chlorides.

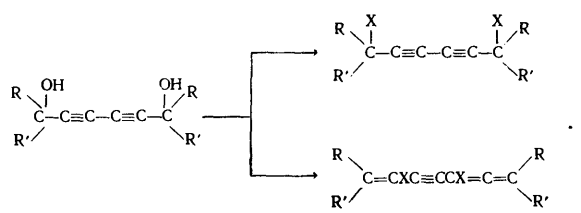
It is interesting to note that in the production of vinylacetylenic bromides only allenic (IV) and trienic (V) bromides are obtained[305]:



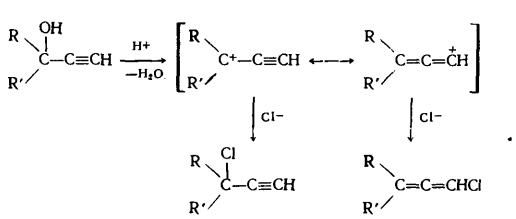
In contrast with this, in the reaction of the vinylacetylenic carbinols mentioned below with hydrogen chloride, thionyl chloride, or phosphorus(III) bromide the reaction passes through an allyl rearrangement[236,249,306-310]:



Diacetylenic glycols react with hydrogen chloride to form diacetylenic and diallenic chlorides[311]:

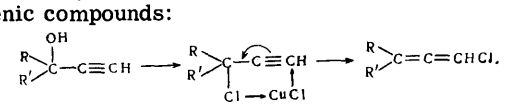


It is interesting that the reaction of hydrogen halides with diethynylquinols also proceeds through a rearrangement[312,313]. Hennion and coworkers[253,314-317] represent the mechanism of the reaction as follows. Under the influence of a proton initially hydroxyl is detached from the alcohol to form a carbonium ion; addition of a chloride anion to the latter leads to the formation of acetylenic and allenic chlorides:

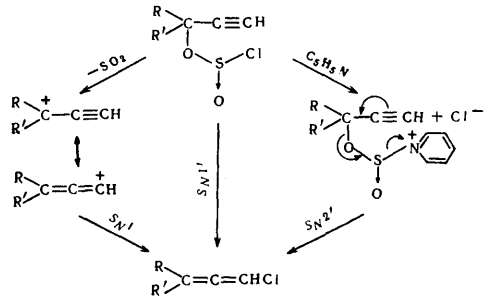


Other authors[302,318,319] regard the isomerisation of chloroalkynes analogously.

The isomerisation of chloroalkynes under the influence of catalysts is improbable, according to Hennion and coworkers[253,315], taking into account the linear structure of acetylenic compounds:

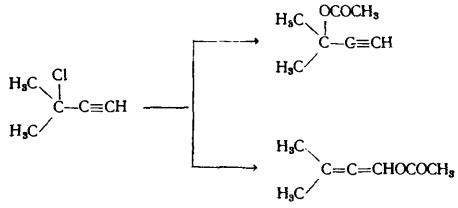


Other authors[259,320] suggest that a chloroalka-1,2-diene can be formed both by an S_N1 and by an S_N2' mechanism:

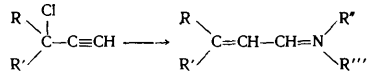


2. Rearrangement on Replacement of the Halogen in α-Halogenoacetylenes

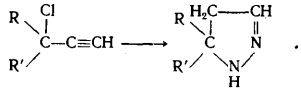
In the nucleophilic replacement of chlorine in α-chloroacetylenes the final product of the reaction is often the corresponding allene compound. Thus in the reaction of sodium acetate with chloroethynyldimethylmethane [3-chloro-3-methylbut-1-yne], in addition to an acetate derivative of acetylene the acetate of allenic alcohol [3-methylbut-1,2-dienyl acetate] is obtained[321]:



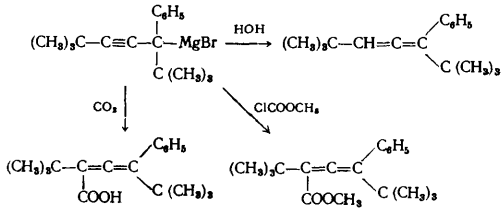
It was found recently that acetylenic chlorides react with substituted hydrazines to form the hydrazones of the isomeric aldehydes[322]:



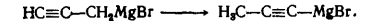
With unsubstituted hydrazine instead of the acetylenic hydrazines 5,5-dialkyl-Δ^2-pyrazolines are obtained[323]:



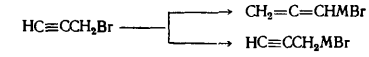
Marvel and coworkers[92] found that during the hydrolysis of an Iotsich complex obtained from an acetylenic chloride instead of the acetylenic hydrocarbon the corresponding allenic hydrocarbon was obtained. The acetylene–allene rearrangement is observed also in the reaction of an Iotsich complex with carbon dioxide or with methyl chloroformate[92]:



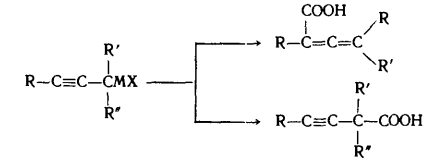
Isomerisation is not observed in the formation of magnesium or sodium derivatives from prop-2-ynyl bromides, but on standing the prop-2-ynylmagnesium complex is isomerised into the prop-1-ynyl complex[324]:



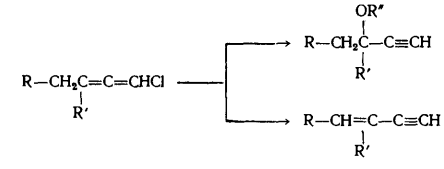
However, in making prop-2-ynylzinc bromide a mixture of acetylenic and allenic derivatives is formed, but with aluminium only a derivative of allene structure is obtained[324,325]:



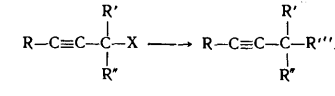
When the prop-2-ynyl Grignard complex reacts with carbon dioxide, a mixture of acetylenic and allenic acids is obtained[324,326-331]:



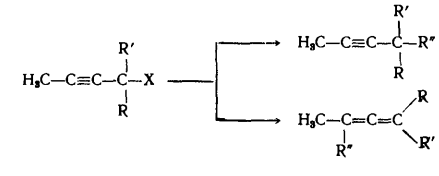
In halogenoalkynes with a halogen atom in β or other positions isomerisation was not observed[332]. It must be noted that an acetylene–allene rearrangement does not occur in the preparation of ethers from the corresponding alkyne chlorides and alcohols in the presence of alkali[314,333] and also in the replacement of halogen in various prop-2-ynyl halides by a variety of agents (amines, alkoxides, salts of acids, sodioacetoacetic ester and sodiomalonic ester[324]). In contrast to this in the replacement of allenic chlorides by a hydroxyl[252,255,333] or alkoxyl[314] group the reaction proceeds with rearrangement:



It was shown that when acetylenic chlorides react with Grignard complexes normal substitution products are obtained[334-336]:

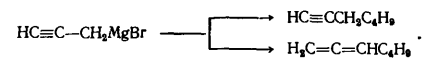


However, in a more detailed study of this reaction, Zakharova noted that in addition to the normal substitution product rearrangement products are obtained—allenic hydrocarbons[337-339]:



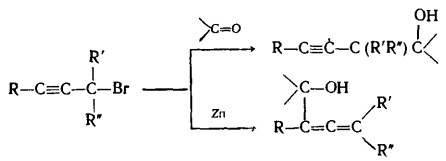
Subsequently the above results were confirmed by other authors[324,340-345] by various examples with primary, secondary, and tertiary acetylenic chlorides. Here allenic hydrocarbons are sometimes the main products of the reaction[346].

The rearrangement also takes place during the reaction of prop-2-ynylmagnesium bromide with dibutyl sulphate[347]:



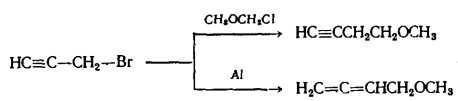
Lithium or sodium acetylides react with benzyl chloride to form allenic compounds[348].

In the presence of zinc acetylenic halides are condensed with aldehydes and ketones with the formation of β-hydroxyacetylenes or -allenes[325,349-351]:

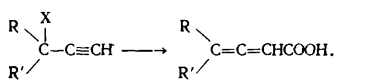


The above halides react similarly with esters[352] and with amides[349] of acids in the presence of metallic magnesium.

It is interesting to note that allenic Grignard complexes under these conditions form mainly acetylenic alcohols[325, 349,353,354]. The complex of prop-2-ynyl bromide with aluminium reacts with chlorodimethyl ether with the formation of a mixture of acetylenic and allenic esters[325]:

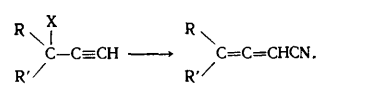


In the reaction of α-halogenoalkynes with tetracarbonylnickel in ethanol or water solution an acetylene–allene rearrangement takes place with the formation of the corresponding allenic acids or their esters[355,356]:

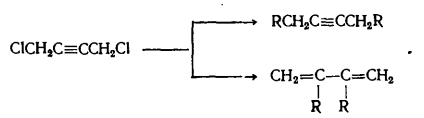


It has been shown that under the same conditions chloroallenes do not react[355], consequently the preliminary rearrangement of chloroacetylenes into chloroallenes and the subsequent course of the reaction is ruled out.

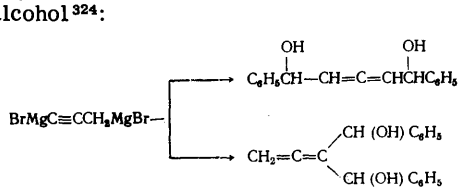
According to patent claims[357] α-halogenoalkynes react with sodium cyanide so that allenic nitriles are obtained:



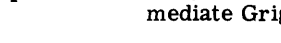
Levina and coworkers[358-360] showed that in the reaction of 1,4-dichlorobutyne with alkylmagnesium bromides a mixture of acetylenic and 1,3-dienic hydrocarbons is obtained:



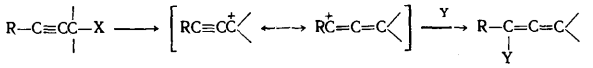
It was also found that the dimagnesium derivative of prop-2-ynyl bromide reacts with benzaldehyde to form an allenic alcohol[324]:



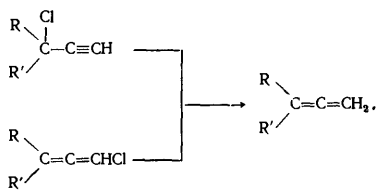
Gaudemar explains the formation of allenic alcohols from acetylenic halides by the prototropic isomerisation of intermediate Grignard complexes[324]:



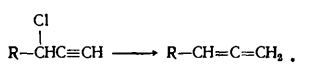
However, in the opinion of many authors the above rearrangements take place through a carbonium ion mechanism according to the scheme[302,324,361]:



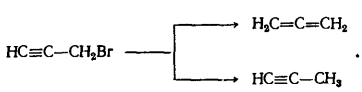
Ginzburg[362,363] showed that in the reduction of α-halogenoacetylenes by zinc instead of the expected acetylenic hydrocarbons allenic ones are obtained. The latter are also obtained in the reduction of allenic chlorides:



Reactions proceed similarly with secondary acetylenic chlorides[364,365]:



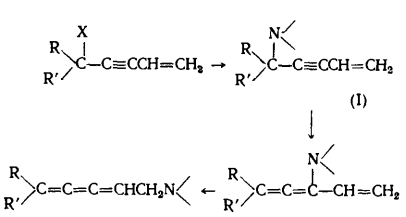
Under these conditions prop-2-ynyl bromide is reduced to a mixture of allene and methylacetylene[273,366,367]:



An analogous reaction is observed in the reduction of chloroacetylenes by metallic zinc, magnesium amalgam and silver, and also by lithium tetrahydroaluminate[75,273, 361,367-369]. Vinylacetylene and diacetylene halides are reduced similarly[370]. Several authors[361,364] have discussed the mechanism of reduction of chloroacetylenes by the above reagents.

IV. ACETYLENE–ALLENE–CUMULENE REARRANGEMENT

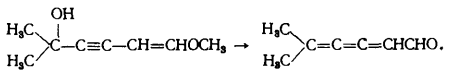
It has recently been found that various vinylacetylenic chlorides smoothly react with amines at room temperature both in the presence of water and also in various solvents: a mixture of vinylacetylenic (I), allenic (II), and cumulenic (III) amines is obtained[371-374]:



It has been found that in the presence of equimolecular amounts of amines the amount of cumulenic amine in the reaction products is increased[372]. The reaction proceeds smoothly at 20–25°C over a few days. It was shown that

under the conditions of the reaction vinylacetylenic and allenic amines undergo rearrangement with the formation of allenic and cumulenic amines.

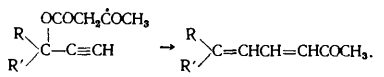
It was found recently that during the slow distillation of a (methoxyvinylethynyl)dimethylcarbinol in the presence of potassium hydrogen sulphate a cumulenic aldehyde is obtained[375,376]:



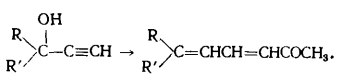
The production of cumulenes from acetylenic and diacetylenic glycols and dihalogen derivatives is another type of rearrangement with participation of the π electrons of the triple bond. There is a review article about this problem[377] so we shall not discuss it.

V. REARRANGEMENT OF ACETOACETATES AND OF ACETATES OF ACETYLENIC ALCOHOLS

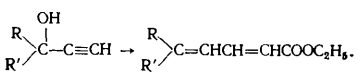
It has been shown that the acetoacetates of acetylenic alcohols are decarboxylated on heating to 160–200°C with the formation of dienic ketones[378,379]:



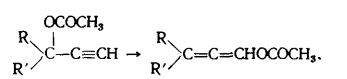
It was found later that this reaction also occurs on the gradual heating of tertiary acetylenic alcohols with acetoacetic ester[380,381]:



Preobrazhenskii and coworkers[382] showed that malonic ester also reacts with acetylenic alcohols, esters of dienic acids being formed as a result:

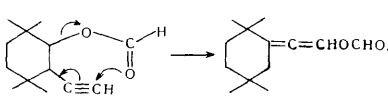


It was also shown that in the pyrolysis of acetates or formates[383–386] of ethynylcarbinols in a steam of nitrogen, acetates of allenic carbinols are obtained as a result of a rearrangement:



The mechanism of the above reaction has been discussed in several papers. Some authors think that it proceeds without the formation of intermediate vinyl esters, others[387–398] explain the formation of the final products through a Claisen rearrangement of the vinyl esters.

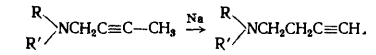
The mechanism of the rearrangement of acetates of acetylenic alcohols has been presented by Landor and Landor[150] as a cyclic process:



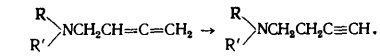
This problem is discussed in greater detail elsewhere[389,390].

VI. REARRANGEMENT OF ACETYLENIC COMPOUNDS CONTAINING OTHER FUNCTIONAL GROUPS

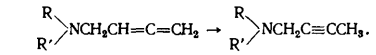
Babayan and coworkers found that 1-dialkylaminobut-2-yne is readily isomerised into 1-dialkylaminobut-3-yne in ethereal solution in the presence of metallic sodium at room temperature[391,392]:



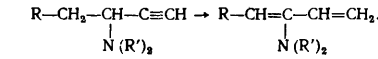
Under these conditions allenic amines also isomerise to form acetylenic amines[393]:



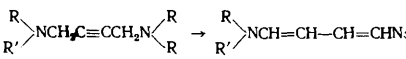
On heating allenic amines in the presence of bases isomerisation proceeds in the reverse direction[394]:



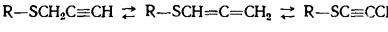
When 3-dialkylaminobut-1-ynes are heated in the presence of aluminium oxide and 1% $Fe(OH)_3$ they are rearranged into the corresponding dienic amines[144,395]:



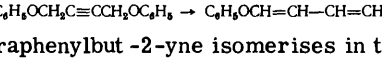
On passing 1,4-bisdialkylaminobut-2-ynes over Cr_2O_3 catalyst[396] at 320–330°C and also in the presence of metallic sodium[397] they are isomerised with formation of the dienic amines:



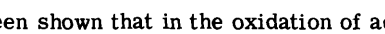
It has been shown that acetylenic thioesters also undergo isomerisation[398] in the presence of bases:



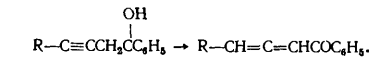
1,4-diphenoxybut-2-ynes are rearranged similarly on heating with potassium t-butoxide[399]:



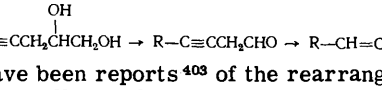
1,1,4,4-Tetraphenylbut-2-yne isomerises in the presence of sodium ethoxide into 1,1,4,4-tetraphenylbuta-2,3-diene[400]:



It has been shown that in the oxidation of acetylenic carbinols or keto-carbinols, instead of the expected acetylenic ketones allenic ketones are obtained[349,401]:

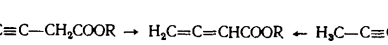


Winter[402] observed similar behaviour in the oxidation of acetylenic glycols with sodium [periodate. (Ed. of Translation)]:



There have been reports[403] of the rearrangement of acetylenic into allenic aldehydes. However, other results[404,405] contradict this.

Johnson and coworkers studied the prototropic conversions of acetylenic acids by many examples. It was shown that prop-2-ynylcarboxylic acid or its esters and also prop-1-ynylcarboxylic acid in the presence of potassium hydroxide is rearranged into an allenecarboxylic acid or its esters[406]:



However, it was found that but-2-yncarboxylic or buta-2,3-diencarboxylic acids are isomerised into but-3-yncarboxylic acid[407]:

$$\left.\begin{matrix} H_3C{-}CH_2C{\equiv}CCOOH \\ H_3C{-}CH{=}C{=}CHCOOH \end{matrix}\right] \rightarrow H_3C{-}C{\equiv}C{-}CH_2COOH.$$

In the presence of amines acetylenic hydroxy-acids are also rearranged into allenic[408]:

$$C_6H_5CHC{\equiv}CCO_2Me \rightarrow \left[C_6H_5C{=}C{=}CHCO_2Me\right] \rightarrow C_6H_5COCH{=}CHCO_2Me.$$

It is curious that in the presence of potassium hydroxide acetylenic alcohols with aromatic substituents are converted into $\alpha\beta$-unsaturated ketones by prototropic rearrangement[409]:

$$(C_6H_5)_2CHC{\equiv}CC_6H_5 \rightarrow \left[C_6H_5C{=}C{=}CHC_6H_5\right]$$
$$C_6H_5COCH_3 + C_6H_5CHO \leftarrow C_6H_5COCH{=}CHC_6H_5$$

It was found that acetylenic acids in which the triple bond is further removed from the carboxyl group undergo rearrangement with formation of the corresponding allenic and dienic acids[407]:

$$R{-}C{\equiv}C{-}CH_2CH_2COOH \rightarrow RCH{=}C{=}CHCH_2COOH \rightarrow RCH{=}CHCH{=}CHCOOH$$

[R = CH_3 (Ed. of Translation)].

In the oxidation of acetylenic glycols with the aid of Cr_2O_3 Jones and coworkers[410] isolated isomeric allenic acids:

$$HOCH_2(CH_2)_nC{\equiv}CCH_2(CH_2)_nCH_2OH \rightarrow HOOC(CH_2)_nCH{=}C{=}CH(CH_2)_nCOOH.$$
$$\uparrow\downarrow$$
$$HOOCCH_2(CH_2)_nC{\equiv}C(CH_2)_nCOOH$$

In the presence of bases vinylacetylenic[350] and diacetylenic[411] acids are converted by a prototropic rearrangement into the corresponding allenic and dienic acids:

$$RC{\equiv}CCH{=}CHCH_2COOH \rightarrow RCH{=}C{=}CHCH{=}CHCOOH$$
$$\left.\begin{matrix} HOOCCH_2C{\equiv}CC{\equiv}CCH_2COOH \\ HOOCC{\equiv}C(CH_2)_2C{\equiv}CCOOH \end{matrix}\right] \rightarrow HOOCCH{=}CHCH{=}CHC{\equiv}CCOOH.$$

The isomerisation of conjugated diacetylenic acids leads to the production of polyenic acids[411]:

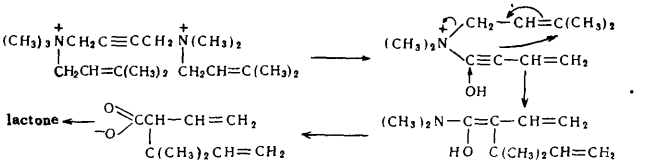
$$HOOC(CH_2)_2(C{\equiv}C)_2(CH_2)_2COOH \rightarrow HOOC(CH{=}CH)_4COOH.$$

It was shown recently that prop-2-ynyl vinyl ethers undergo a Claisen rearrangement as follows[412]:

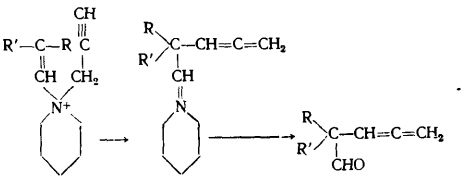
$$CH_2{=}CHOCH_2C{\equiv}CH \xrightarrow[CO_2]{C_2H_5MgBr} HOOCC{\equiv}CCH_2OCH{=}CH_2$$
$$\downarrow$$
$$HOOC{-}\underset{\|}{C}(CH{=}O){-}CH{=}CH_2 \leftarrow HOOC{-}\underset{|}{C}(CH_2CHO){=}C{=}CH_2$$
$$\downarrow\uparrow$$
$$H_2C{=}CH\underset{\|}{C}(CH{-}OH){-}\underset{|}{C}{=}O$$

According to some investigators[412,413], other prop-2-ynyl vinyl ethers undergo this reaction, particularly the prop-2-ynyl acetal of isobutyraldehyde. It was also shown that the 1,4-bisdiphenyl esters of but-2-yn-1,4-diol undergo a Claisen rearrangement when heated in diethylaniline[414].

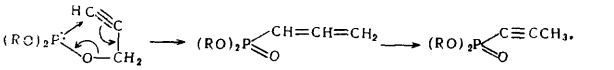
Babayan and coworkers[415] showed that quaternary ammonium bases which contain $\beta\gamma$-acetylenic and allyl radicals form acids or the corresponding lactones under the influence of aqueous alkalis, by the scheme:



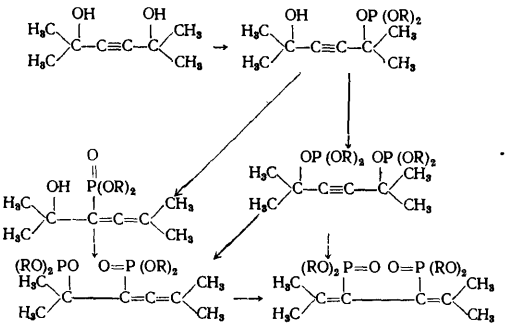
According to the result of Opitz[416], prop-2-ynyl vinyl bases undergo a Claisen rearrangement with the formation of intermediate enamines which are hydrolysed into allenic aldehydes:



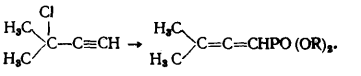
Pudovik and coworkers[417] showed that dialkyl-$\beta\gamma$-propynyl phosphites isomerise on standing into the dialkyl esters of $\alpha\beta$-propynylphosphinic acids:



It has been shown that phosphoric esters of butyndiols[418,419] also undergo the rearrangement described above:



Analogous results were obtained in the reaction of chloroethynyldimethylmethane [3-chloro-3-methylbut-1-yne] with a trialkyl phosphite[420]:



An acetylene–allene rearrangement was observed in the reaction of acetylenic carbinols with R_1R_2PCl, R_1PCl_2, PCl_3.[421] Allenic and acetylenic esters of phosphonic acids readily undergo prototropic isomerisation on heating in the presence of a catalytic amount of sodium ethoxide[422]:

$$RCH{=}C{=}CHPO(OR)_2 \rightarrow RCH_2C{\equiv}CPO(OR)_2,$$
$$CH{=}CH{-}C{\equiv}CCH_2PO(OC_2H_5)_2 \rightarrow CH_3CH{=}CHC{\equiv}CPO(OR)_2.$$

The authors state that these rearrangements proceed more smoothly than the rearrangement of the corresponding ethylene esters of phosphoric acid[423].

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C-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

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I. INTRODUCTION

From the time it was established that cellulose is a high-molecular-weight polysaccharide, the elementary unit of which contains alcoholic hydroxyls, investigations in the field of cellulose chemistry were directed mainly towards the study of the reactions involving replacement of the hydrogen atoms of the hydroxyl groups by acyl and alkyl radicals, that is, reactions of *O*-acylation and *O*-alkylation. The interest in obtaining cellulose ethers and esters is due to their widespread use in various products. Existing reviews and monographs mainly survey the progress in the field of the preparation and investigation of the properties of *O*-derivatives of cellulose. Even in the reviews which have appeared recently, in addition to such problems of cellulose chemistry as the dependence of the reactivity of cellulose on its physical structure and the comparative reactivity of the hydroxyl groups in alkylation and acylation, only problems arising in connection with the preparation of cross-linked cellulose macromolecules and graft copolymers of cellulose are considered[1,2].

The present review considers the development of the chemistry by the *C*-derivatives of cellulose, in which the hydroxyl groups are replaced by other functional groups. After the publication of the last monographs on cellulose chemistry[3,4] a number of new syntheses of aminodeoxy- and halogenodeoxy-celluloses have been effected. Hydrazino-, thiocyanato-, nitro-, mercapto-, and other new *C*-derivatives of cellulose have now been obtained.

The chemistry of the *C*-derivatives of cellulose is of great theoretical interest for the further study of the structure of cellulose. It allows a large number of reactions to be used for studying the glucopyranose unit. The investigation of the properties of *C*-derivatives of cellulose with a specified position of a substituent in the elementary unit allows information to be obtained about the carbon atom at which a given substituent is located. This will evidently facilitate an understanding of the complex problems of the mutual influence of groups in carbohydrates and the induction effects acting in them.

The practical interest in the chemistry of *C*-derivatives of cellulose consists both in the modification of cellulose materials with the aim of discovering new possibilities for their use, and also in the search for new ways of using cellulose as an organic raw material.

II. AMINO-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

Attempts to replace the hydroxyl groups in cellulose and starch by amino-groups were made about 75 years ago[5], but the interest in this problem has never waned since then. Amination was carried out with the aim of increasing the dyeability of cellulose fibres[6,7], and for the production of

anion-exchange materials[8] or of analogues of chitosan and chitin[9].

1. Reactions Used for Introducing Amino-Groups into Polysaccharides

Several reactions have been used for obtaining amino-derivatives of cellulose and other polysaccharides.

a. The action of ammonia on cellulose- and acetylcellulose-esters of sulphonic acids:

$$C_6H_7O_2(OH)_{3-x}(OSO_2R)_x \xrightarrow{NH_3} C_6H_7O_2(OH)_{3-x}(OSO_2R)_{x-y}(NH_2)_y.$$

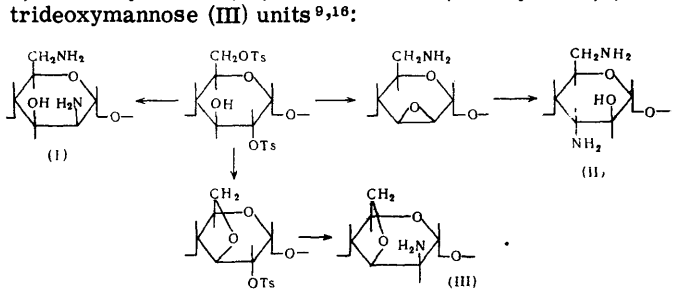
On boiling cellulose *p*-toluenesulphonate (tosylcellulose) with a concentrated solution of ammonia for 1 h at 100°C, Karrer and Wehrli[10] introduced 0.7–0.8% nitrogen into cellulose. On investigating the same reaction Sakurada[11,12] concluded that it only takes place to a slight extent. Gardner[13] also did not succeed in introducing an appreciable amount of nitrogen into cellulose by the action of ammonia on its mixed ester containing tosyl and acetyl groups. During the process the cellulose underwent considerable degradation.

By carrying out the reaction at room temperature or heating cellulose methanesulphonate (mesylcellulose) containing from 0.5 to 1 mesyl group per unit with an aqueous solution of ammonia (28–29%), part of the mesyl groups could be replaced. The products contained 0.5–4% nitrogen and 3–6% sulphur. A change in the reaction conditions did not yield a product free from sulphur[14]. An aminocellulose with 2.5–4.2% nitrogen, 12–14% sulphur, was obtained on treating mesyl cellulose (γ = 150–170) with a solution of ammonia in methanol[15].

b. Reaction of amylose *p*-toluenesulphonate with hydrazine or sodium hydrazide, with subsequent reduction:

$$C_6H_7O_2(OH)_{1.3}(OSO_2C_6H_4CH_3)_{1.7} \xrightarrow{NH_2NH_2} C_6H_7O_2(OH)_{1.6}(NHNH_2)_{1.4} \xrightarrow{NaNO_2} C_6H_7O_2(OH)_{1.6}(N_3)_{1.4} \rightarrow C_6H_7O_2(OH)_{1.6}(NH_2)_{1.4}.$$

The replacement of a considerable proportion of the hydroxyl groups in a polysaccharide by amino-groups was achieved in the reaction of tosylamylose (γ = 170) with hydrazine followed by reduction of the reaction product. To obtain the hydrazinoamylose, ditosylamylose was boiled for 7 days with anhydrous hydrazine under nitrogen. The hydrazinoamylose was reduced to aminoamylose in aqueous solution by Raney nickel for 24 h. The aminoamylose obtained (γ = 140) is an absolutely inhomogeneous product containing, in consequence of the reaction having proceeded in various directions, both 6-amino-6-deoxyglucopyranose and also 2,6-diamino-2,6-dideoxymannose (I), 3,6-diamino-3,6-dideoxyaltrose (II), and 2-amino-3,6-anhydro-2,3,6-trideoxymannose (III) units[9,16]:



6-Amino-6-deoxyamylose with a degree of substitution of 0.1–1 was obtained through the 6-amino-derivative with protected secondary hydroxyl groups by the following scheme[17]:

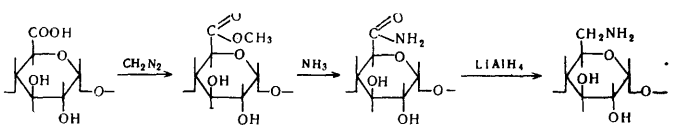
amylose
↓
6-*O*-tritylamylose
↓
6-*O*-tritylamylose 2,3-di-*O*-phenylcarbamate
↓
amylose 2,3-di-*O*-phenylcarbamate
↓
6-azido-6-deoxyamylose 2,3-di-*O*-phenylcarbamate
↓
6-amino-6-deoxyamylose.

c. Reduction of cellulose nitrate by sodium amide:

$$C_6H_7O_2(OH)(ONO_2)_2 \xrightarrow{NaNH_2} C_6H_7O_2(OH)_2(NH_2).$$

By reducing cellulose nitrate (11.7% nitrogen) with sodium amide in liquid ammonia for 9 h, Scherer and Feild[18] obtained monoaminocellulose, with 8.35% total and 7.94% amine nitrogen, which was evidently extensively degraded, as it was extremely soluble in water.

d. Reduction of the amide of an alginic acid:



A new attempt was recently made to introduce an amino-group into a polysaccharide by making use of the reduction of an acid amide. The degree of esterification of the alginic acid and the number of amido-groups introduced were sufficiently high but the product obtained on reducing the amide with lithium tetrahydroaluminate only contained 12 amino-groups per 100 glucose residues[19].

e. Action of ammonia on halogenodeoxycellulose:

$$C_6H_7O_2(OH)_{3-x}(hal)_x \xrightarrow{NH_3} C_6H_7O_2(OH)_{3-y}(NH_2)_y.$$

It has proved impossible to introduce into cellulose an appreciable amount of nitrogen by treating acetyl-6-iodo-6-deoxytosylcellulose with ammonia in organic solvents; a little nitrogen (0.3%) was introduced into it on using sodium amide in liquid ammonia[13]. Recently, Polyakov and Rogovin[8] reinvestigated this reaction. As a result of treating chlorodeoxycellulose with ammonia in alcoholic solution at 160°C they succeeded in introducing 23 amino-groups per 100 glucose residues, which corresponded with 2.25% nitrogen. Under the action of aqueous ammonia saponification of the chlorine occurred in addition to the substitution.

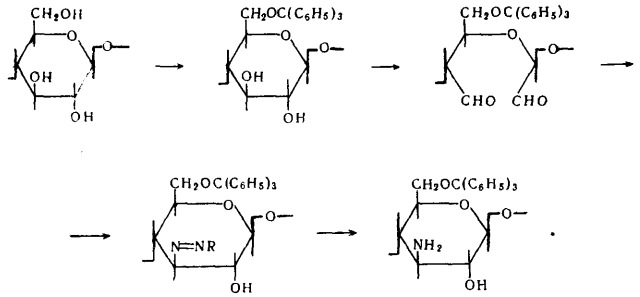
f. Phthalimide synthesis.

An attempt was made to replace a tosyl group in cellulose and acetylcellulose by a phthalimide residue. It was suggested that on saponification of the phthaloyl derivative an aminocellulose and phthalic acid would be obtained.

Only 25% of the tosyl groups in 2,3-di-*O*-acetyl-6-*O*-tosylcellulose could be replaced. In acetyltosylcelluloses with 1.85 acetyl and 0.43 tosyl groups per elementary unit of the cellulose, the tosyl groups were replaced stoichiometrically by the phthalimido-groups. However, it was

found impossible to remove the phthalic acid residues and obtain aminocellulose in this way[20].

g. Condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine and reduction of the condensation product[21,22]:



The condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine in pyridine solution for 24 h gave partially and completely substituted 3-deoxy-3-*p*-tolylazo-6-*O*-tritylcellulose. Reduction of the condensation product in the presence of Raney nickel at a hydrogen pressure of 150 atm and 90°C yielded 3-amino-3-deoxy-6-*O*-tritylcellulose with various amino-group contents, for example:

$$C_6H_7C_2(CH)_{1.46}(NH_2)_{0.62}[CC(C_6H_5)_3]_{0.92}.$$

Hence despite the many stages in the processes, the incompleteness of the reactions, and the great difficulty in proving the structure of the products obtained, the search for new syntheses of aminopolysaccharides is still continuing. The greatest degree of conversion into aminopolysaccharides was reached during the introduction of hydrazido- or azido-groups into tosylamylose and their subsequent reduction. Of all the reactions used, only the condensation of 2,3-aldehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine and subsequent reduction of the product allows an amino-group to be introduced into the glucopyranose chain of cellulose in a definite position: at the third carbon atom.

2. Properties of Aminodeoxypolysaccharides

Aminocellulose is soluble in water, capable of being diazotised and of forming dyes on combination with 1-naphthol, 2-naphthol, aniline, resorcinol, phenol, *o*-cresol, 1-naphthylamine, 2-naphthylamine, etc. It is uncertain, however, whether the dyes produced have the diazo-structure since they are stable to reduction and nitration[23].

Deacetylated chitin and desulphated heparin are deaminated under the action of nitrous acid[24,25].

The exchange capacity of aminocellulose with a high concentration of amino-groups is 2.5 mg-equiv. g^{-1}.[8]

The chemical properties of the glucoside bond and of hydroxyl groups when amino-groups are present in the polysaccharide have been studied in detail, by the example of chitosan and chitin[26]. Danilov and Plisko investigated the action of acids and alkalis on chitin and also its reactivity in etherification and alkylation. The chitin is dissolved in dilute organic and mineral acids after swelling in 8–10% sodium hydroxide at −40°C. Glyceryl, hydroxyethyl, ethyl, and carboxymethyl ethers of chitin were obtained[27–30]. Note that chitin is less reactive than cellulose (as was shown earlier[31–33]) in the reactions for the formation of ethers and esters[34].

N-alkyl and *N*-aryl derivatives of aminocellulose were obtained indirectly[6,7,8,20,35–40]. They dissolve in organic solvents[36] and dilute solutions of acetic acid, and are capable of forming fibres with the best dyability with acid dyes. There are indications that it may be possible to use them as finishes, protective coatings, photographic film base, etc.[41]

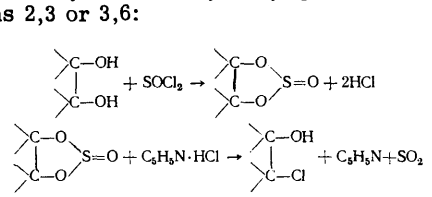
Aminocellulose exhibits increased affinity for acid dyes[6,7] and it is capable of being formed into threads from solution in acetic acid in an alkaline bath[42]. Aminocellulose and aminostarch are mentioned as basic polysaccharides which can be used for finishing fibres[35].

III. HALOGEN DERIVATIVES OF CELLULOSE

The introduction of halogen into cellulose has two aims: modification of the cellulose and the production of reactive derivatives for further syntheses[43].

1. Reactions Used for Introducing a Halogen into Cellulose

a. The reaction of cellulose with thionyl chloride. As long ago as 1931, Carré[44] obtained a substance of composition $C_6H_9O_4Cl$ by the action of thionyl chloride in pyridine on cotton linter. Recently a more detailed study was made both of the reaction itself and of the products obtained. The influence of time and temperature on the degree of substitution of chlorodeoxycellulose[45] was investigated and it was shown that replacement of pyridine by a more polar solvent, for example, dimethylformamide, accelerates the reaction[8]. Chlorodeoxycellulose obtained in pyridine or dimethylformamide at elevated temperatures is dark cinnamon-brown. Carrying out the reaction in carbon tetrachloride or chloroform at the boiling point of the solvent allows a colourless chlorodeoxycellulose to be obtained[46]. The presence of iron accelerates the reaction, especially in carbon tetrachloride. During the preparation of chlorodeoxycellulose in pyridine, hydrolysis of the cellulose takes place, which becomes apparent in a drop in its tensile strength[44]. Chlorodeoxycellulose obtained in pyridine contains sulphur, possibly as sulphate esters. The sulphur concentration depends on how the chlorodeoxycellulose is treated at the end of the reaction: with dilute alkali, sodium chlorite, sodium hydrogen carbonate, or methanol[45]. The possibility of the formation of elementary units with anhydro-rings on carrying out the reaction either in pyridine[45] or in dimethylformamide[8] is not ruled out. Chlorodeoxycellulose obtained in a medium of chloroform or carbon tetrachloride did not contain sulphur and anhydro-rings; hydrolysis of cellulose did not take place during its preparation[46]. Two mechanisms for the formation of chloro-substituted cellulose using thionyl chloride in pyridine have been suggested. In the first of these it is assumed that there are intermediate cyclic sulphate esters which are formed by the reaction of thionyl with the hydroxyl groups of the cellulose in positions 2,3 or 3,6:



The second mechanism presupposes the formation of an intermediate unstable ester of chlorosulphurous acid:

$$ROH + SOCl_2 \rightarrow ROSOCl + HCl$$
$$ROSOCl \rightarrow RCl + SO_2.$$

The first mechanism is supported by the fact that chlorodeoxycellulose is obtained under the conditions for the tosylation of cellulose where the chlorinating agent can only be pyridinium chloride:

$$C_6H_7O_2(OH)_2(OSO_2C_7H_7) + C_5H_5N\cdot HCl \rightarrow$$
$$\rightarrow C_6H_7O_2(OH)_2(OSO_2C_7H_7)_{1-x}Cl_x + C_5H_5NHSO_2C_7H_7,$$

and also by the fact of the formation of cyclic sulphites from polyhydroxy-compounds[47-49] and by the presence of stably-bound sulphur in chlorodeoxycellulose.

The second mechanism finds support from the results of a detailed investigation of the reaction of simple alcohols with thionyl chloride[50-52].

b. Nucleophilic substitution in the reaction of cellulose sulphonates and nitrates with salts of hydrohalogen acids. An exhaustive review[53] on the reactivity of cellulose sulphonates (particularly in reacting with alkali metal halides) has been published.

The specificity of this reaction, namely, the replacement first of all of the tosyl group at the primary carbon atom, was first shown with galactose[54].

A polysaccharide containing a halogen at $C_{(6)}$, 6-deoxy-6-iodo-2,3-ditosylstarch, was first obtained by the action of sodium iodide on tritosylstarch in acetone at 100°C for 3 days[55-57].

Cramer and Purves[58] were the first to replace a primary tosyl group in cellulose by iodine; they used a preparation of partially saponified triacetylcellulose[58]. Then a series of papers were devoted to the use of this reaction for studying the distribution of tosyl groups between the primary and secondary carbon atoms of the elementary unit of cellulose[59-61]. Despite the fact that tosyl groups at secondary carbon atoms are also replaced by halogen[60,62], as was noted above, this reaction has also repeatedly been used for studying the structure of various derivatives of cellulose[63-69] and other polysaccharides[70]. It was shown recently that on carrying out the reaction in a polar solvent not only tosyl groups at the primary but also those at secondary carbon atoms are replaced by halogen[71]. Halogenocellulose free from sulphur was obtained on replacing a methanesulphonate group in a mixed cellulose ester containing acetyl and mesyl groups by iodine (the cellulose ester was treated with sodium iodide). The product contained 0.4 atom of iodine per elementary unit of the cellulose. The initial content of mesyl groups was 0.9.[13]

A method for the introduction of I, Br, Cl, and F into cellulose by the reaction of alkali metal salts and hydrohalogen acids with mesylcellulose in aqueous medium, not in organic solvents, has been developed[72].

In the nucleophilic replacement of a nitrate group by iodine, on treating partially nitrated cotton cellulose with sodium iodide in ethyl methyl ketone for 12 h at 115°C iodine-containing cellulose nitrate was obtained (33% iodine and 0.7–2.5% nitrogen; initial nitrogen content 2.5–9.0%).

By analogy with the monosaccharides it is thought that the iodine replaces only the primary nitrate groups[73]. This reaction is used for studying the distribution of substituents in the elementary unit of cellulose derivatives[74,75]. An insignificant drop in temperature significantly retards the reaction. On using zinc, calcium, or barium iodide under the same conditions only 0.2–2.8% iodine could be introduced into cellulose[73].

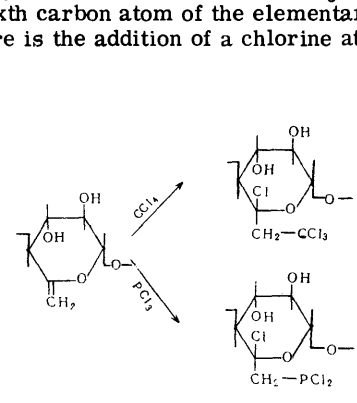
In comparing the reactivity of tosyl, nitrate, and sulphate esters of cellulose in reactions with halides it was found that with lithium chloride or potassium bromide the tosyl ester is most reactive and cellulose sulphate does not react. In reactions with sodium iodide the difference in the reactivity of cellulose *p*-toluenesulphonate and nitrate is less noticeable[76]. It was shown that as a result of side-reactions the ester groups are removed without the introduction of halogen[73,76].

c. Reaction of cellulose phosphinates with alkyl halides:

$$C_6H_7O_2(OH)_3 \xrightarrow{(C_2H_5)_2NP(C_2H_5)_2} C_6H_7O_2(OH)_{3-x}[OP(C_2H_5)_2]_x \xrightarrow{C_6H_5CH_2Cl}$$
$$\rightarrow C_6H_7O_2(OH)_{3-x}Cl_x.$$

A new method of obtaining deoxyhalogenocelluloses by the reaction of cellulose diethylphosphanate with benzyl chloride was recently developed. As a result of a fivefold treatment of a cellulose ester with 4% phosphorus ($\gamma = 30$), with benzyl chloride for 4 h at 120–130°C a chlorodeoxycellulose with 4% chlorine was obtained[77].

d. Addition of CCl_4 and PCl_3 at a double bond. There is a report of the preparation of 5-chloro-6-deoxycellulose starting from cellulose-5,6.[78] Here simultaneously with the addition of the CCl_3 and PCl_2 radicals to the sixth carbon atom of the elementary unit of cellulose there is the addition of a chlorine atom to the fifth carbon atom:



2. Properties of Deoxyhalogenocelluloses

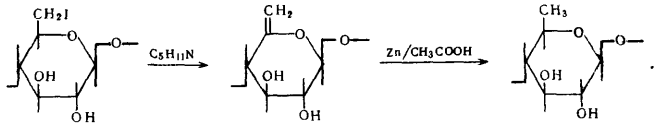
a. Structure and properties. An attempt was made with the aid of paper chromatography of the hydrolysis products to determine the position of chlorine in chlorodeoxycellulose obtained by the action of thionyl chloride in pyridine on cellulose. A specimen of chlorodeoxycellulose containing 6% chlorine was investigated. It was shown that 22% of the chlorine is at $C_{(6)}$. 6-Chloro-6-deoxyglucopyranose was isolated and characterised in this way, but the composition of the other four fractions was not studied. It is suggested that they can contain 2- or 3-monosubstituted glucose, mannose, and allose, and also 2,3- and 3,6-anhydro-derivatives of the same monosaccharides. It was noted that the chlorine in the chlorodeoxycellulose is resistant to saponification under conditions of complete hydrolysis of the latter at the glucoside bonds by 72% sulphuric acid. The introduction of halogen into the cellulose also raises the resistance of the glucoside

bonds to hydrolysis: with increase in the degree of substitution there is an increase in the amount of the unhydrolysable part[45].

On treating the chlorodeoxycellulose with concentrated aqueous solution of ammonia, in addition to the replacement of halogen by an amino-group 50% of the chlorine is saponified. When treated with an alcoholic solution of ammonia, saponification does not take place[8].

Iodine- and bromine-containing mesylcelluloses show enhanced resistance to combustion compared with the initial mesitylcellulose. The introduction of chlorine has no effect on the stability of mesylcellulose to combustion, but the introduction of fluorine impairs it[72].

b. Reactions of deoxyhalogenocelluloses. When pyridine acts on 6-deoxy-6-iodo cellulose (γ = 70), HI is lost and the cellulos-5,6-ene formed. By reduction of an unsaturated derivative of cellulose with zinc in acetic acid, a completely saturated compound is obtained, 6-deoxycellulose[79]:



Cyanodeoxycellulose was obtained by the reaction of chlorodeoxycellulose with potassium cyanide in dimethylformamide or methanol at elevated temperatures. Under the conditions used not more than 65% of the chlorine atoms are replaced. When even a little water (1–1.5%) is present in the reaction mixture, gradual saponification of the nitrile groups takes place[8].

$$C_6H_7O_2(OH)_{2.37}Cl_{0.63} \xrightarrow{KCN} C_6H_7O_2(OH)_{2.59}(CN)_{0.41}.$$

A solution of sodium hydrazide in absolute hydrazine or liquid ammonia (in nitrogen atmosphere) acts on chlorodeoxycellulose to give deoxyhydrazinocellulose. It is possible that there is the parallel formation of anhydrides, since there was some disagreement between the proportion of chlorine atoms removed and the content of hydrazino-groups:

$$C_6H_7O_2(OH)_{2.37}Cl_{0.63} \rightarrow C_6H_7O_2(OH)_{2.37+(0.63-x)}(NHNH_2)_x.$$

IV. HYDRAZINO-, THIOCYANATO-, NITRO-, MERCAPTO-, AND OTHER DEOXY-DERIVATIVES OF CELLULOSE; PREPARATION AND PROPERTIES

Deoxyhydrazinocellulose with a 0.16–0.88 substitution was obtained on the reaction of a solution of sodium hydrazide in absolute hydrazine with tosyl or mesyl esters of cellulose containing 0.44–1.71 sulphonate groups per elementary unit of the cellulose. The reaction was carried out at 20° and –33°C for 15–72 h [80]. Whistler and Shasha[81] obtained 6-deoxy-6-hydrazinocellulose from 6-*O*-tosylcellulose with a degree of replacement of 0.64 by treatment with hydrazine for 30 min at 100°C. Viscosimetric measurements showed that hydrazinolysis took place to an insignificant extent under the conditions of the experiment.

Note that not all the tosyl groups are replaced by hydrazine residues. Since the deoxyhydrazinocellulose did not contain sulphur, evidently part of the tosyl or mesyl groups are saponified under the conditions of the experiment.

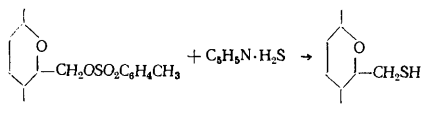
Highly substituted deoxyhydrazinocelluloses (γ = 70–80) are soluble in water and dilute acids, but do not dissolve in alcohol or acetone[80]. The hydrochloride of 6-deoxy-6-hydrazinocellulose is stable and dissolves in water to form a transparent, stable solution. Oxygen, hydrogen peroxide, nitrous acid, iodine, and potassium iodide oxidise the free base[81]. Fabric based on deoxyhydrazinocellulose is readily dyed by acid dyes and absorbs from 1.5 to 1.7 moles hydrochloric acid per hydrazino-group[80]. A deoxy(phenylhydrazino)cellulose with degree of substitution 1–1.35 was obtained on the basis of ditosylcellulose. This preparation also contained from 0.61 to 0.96 tosyl groups per elementary unit of the cellulose. Deoxy(phenylhydrazino)cellulose is soluble in dimethylformamide and does not dissolve in acetone, chloroform, or methanol[80].

Deoxynitrocellulose was obtained by the nucleophilic replacement of tosyl groups in tosylcellulose. The tosylcellulose (γ = 100–180) was treated with sodium nitrite in water and in dimethylformamide for different periods at temperatures from 20° to 140°C. All the tosyl groups could not be replaced. The cellulose derivatives obtained contained both tosyl and nitro-groups. The maximal degree of substitution was 0.4 for nitro-groups[82]:

$$[C_6H_7C_2(CH)_{1.96}(OSO_2C_6H_4CH_3)_{0.62}(NC_2)_{0.42}]_n.$$

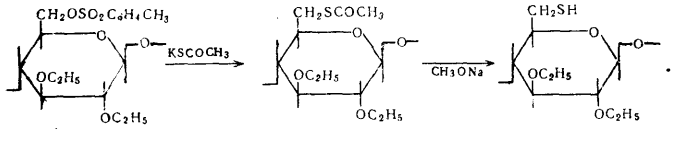
Thiocyanatocellulose (γ = 100) was obtained by the action of sodium or potassium thiocyanate on ditosylcellulose for 8–10 h [59,71]. Partially substituted deoxythiocyanatocellulose was obtained from cellulose nitrate. The maximal degree of substitution of ester groups by thiocyanato-groups under these conditions was 42%.[83]

Deoxymercaptocellulose was obtained by the action of hydrogen sulphide in pyridine on a mixed ester of cellulose containing acetyl (2.44 per elementary unit) and tosyl (0.35 per elementary unit) groups. 80% of the tosyl groups were replaced by mercapto-groups in 8 hours at 35–40°C. When the reaction product,



which is soluble in acetone, was held in air or treated with iodine, it lost its solubility, owing to the formation of disulphide bridges between the cellulose macromolecules[84].

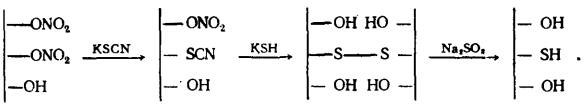
A small number of mercapto groups (0.16 per elementary unit) was introduced into cellulose by the action of potassium thioacetate on a mixed cellulose ester containing ethoxy- and tosyl groups with subsequent deacetylation. The product is soluble in acetone, but in air it oxidises readily, being converted into an insoluble cross-linked polymer[85]:



A cotton cellulose with mercapto-groups was obtained similarly[86].

By passing hydrogen sulphide through a solution of ditosylcellulose in dimethylformamide from 0.5 to 1.79 mercapto-groups could be introduced into the cellulose (calculated per elementary unit)[71].

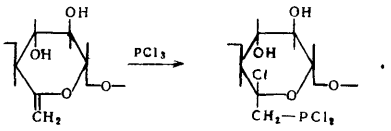
A cellulose derivative containing mercapto-groups was also obtained by the denitration of deoxythiocyanatocellulose nitrate with subsequent reduction[83]:



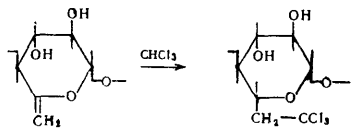
Phosphorus-containing deoxycellulose is formed by the reaction of tosylcellulose with sodium diethyl phosphite[87]:

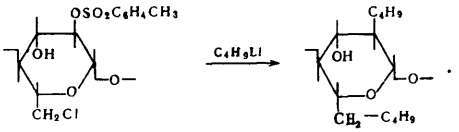
$$\text{cell}-OSO_2C_6H_4CH_3 + NaPO(OC_2H_5)_2 \rightarrow \text{cell}-PO(OC_2H_5)_2 .$$

An original reaction of radical addition of phosphorus trichloride to a cellulose-5,6-ene has been described[78]:

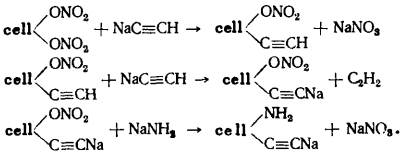


Alkyldeoxycellulose. Papers appeared recently on two methods of introducing alkyl radicals into the glucopyranose unit of cellulose[78,88]:



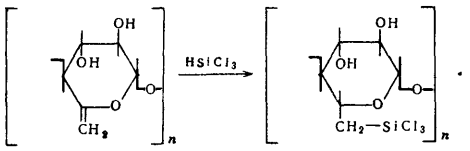


Ethynyldeoxycellulose. As a result of the reaction of cellulose nitrate (11.9% nitrogen) with sodium acetylide in liquid ammonia, a product is obtained with one acetylene and one amino-group for each elementary unit of cellulose:



The acetylene derivative of cellulose in the preparation is readily soluble in liquid ammonia and is not precipitated by water and alcohol. However, after evaporating off the ammonia the product loses its solubility, both in ammonia and in organic solvents, probably because of polymerisation at the acetylene groups[89].

Silicon-containing deoxycellulose is obtained as a result of the following reaction[78]:



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Despite the fact that the chemistry of the *C*-derivatives of cellulose began to develop a long time ago and that interest in it has intensified recently, it is noteworthy that even the most serious investigations have not been pursued to the end. Many authors considered it sufficient to show just the possibility in principle of some particular reaction.

There is a need for further development of the investigations in the field of *C*-derivatives of cellulose, both to seek for new reactions and to find conditions under which these reactions would proceed as completely as possible and not be accompanied, if possible, by various side-processes and by the change in the configuration of the elementary unit of cellulose.

There is special interest in specific reactions which would ensure the production of cellulose derivatives with a definite position of a substituent in its elementary unit. New reactions, for example, the condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine[21,22] and the radical addition of a series of compounds to cellulose-5,6-ene[78], show that possibilities in this direction are far from exhausted.

The study of the properties of *C*-derivatives of cellulose can be considered an almost untouched field of investigation.

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U. D. C. 535.34

THE ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF *N*-HETERO-AROMATIC COMPOUNDS AND THEIR DERIVATIVES

R. N. Nurmukhametov

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1. GENERAL REMARKS

In recent years considerable progress has been made towards establishing the relationship between the structure and the spectroscopic-luminescent properties of polyatomic organic molecules. This progress is due to the mutual enrichment of theoretical and experimental studies. The work of a large number of experimentalists, using the results of theory, has revealed comparatively simple and general features, which reflect the relationship between spectra and structure and for which theoretical papers have given further qualititative or semi-quantitative explanations based on an examination of successfully chosen approximations and models. The *N*-hetero-aromatic compounds form one class of compound for which important results have been obtained.

N-Heteroaromatic compounds differ formally from aromatic hydrocarbons in that a =CH– group has been replaced by =N– in the aromatic ring. Since the π-system is preserved, it might be expected that the absorption spectra of *N*-heterocyclic compounds would contain bands similar to chose of the hydrocarbon analogues and due to $\pi-\pi^*$ transitions (excitation of an electron from a filled bonding π-orbital of an unoccupied antibonding π^*-orbital). Such bands are in fact observed, although the intensities and positions are slightly different, because of the inductive effect of the N atom and the decreased symmetry of the molecule. In addition to these bands, the spectra of *N*-heterocycles contain other less intense bands due to $n-\pi^*$ transitions (excitation by promotion of an electron of an unshared pair from the non-bonding orbital of the N atom to an antibonding π^*-orbital). The bands due to $n-\pi^*$ transitions are clearly distinguished in the spectrum only when they are the bands with longest wavelength. The assignment of the bands to $\pi-\pi^*$ and $n-\pi^*$ transitions and the classification of the bands of aza-heterocycles and other organic compounds, based on this assignment, were developed in a paper by Kasha[1].

Goodman made a systematic experimental and theoretical study of the electronic spectra of azines, and summarised the results in a review[2], in which he put forward a theory to explain the energies of the transitions, their intensities, and the singlet-triplet splitting. Mason[3-6] made a systematic study of the position and intensities (oscillator strengths) of the π, π^* and n, π^* absorption bands for various *N*-heterocyclic aromatic compounds. Clementi and Kasha[7] examined the problem of spin-orbital coupling in the n, π^*-state of *N*-heterocycles; this was subsequently developed by El-Sayed[8].

The n, π^*- and π, π^*-states show significantly different luminescent properties, which therefore depend on the relative arrangement of the singlet and triplet n, π^*- and π, π^*-levels. For this reason, the luminescent properties of aza-aromatic compounds differ from those of the corresponding hydrocarbon analogues. Aromatic hydrocarbons exhibit fluorescence and phosphorescence, whereas many *N*-heterocycles are non-fluorescent.

If the spectroscopic-luminescent properties of molecules depend on the relative arrangement of the n, π^*- and π, π^*- levels, this arrangement is determined by the structure of the molecules. The similarity in the π, π^*- bands of *N*-heteroaromatic compounds and their hydrocarbon analogues, demonstrated by Zanker[9], makes it possible to transfer the relationships known for the π, π^*-bands of aromatic hydrocarbons to the corresponding *N*-heterocycles.

The empirical relationships between the structure and spectra of aromatic polynuclear condensed hydrocarbons[10] are found to be applicable for the π, π^*-bands of *N*-heterocyclic compounds. These relationships facilitate the examination of the electronic spectra of these compounds. A general feature of triplet-singlet ($T-S_0$) transitions in aromatic hydrocarbons is that they exhibit polarisation perpendicular to the plane of the molecule. Dorr[11,12], who established this characteristic feature, showed that it also applies to the $T-S_0$ transitions of the π, π^* phosphorescence of *N*-heterocyclic compounds. El-Sayed and Brewer[13] showed for various *N*-heterocycles that the n, π^* phosphorescence exhibits polarisation in the plane of the molecule whereas the π, π^* phosphorescence exhibits polarisation perpendicular to the plane of the molecule. Zimmerman and Joop[14] showed that the polarisation of the π, π^*-bands for the absorption and fluorescence of *N*-heterocycles is the same as that for their hydrocarbon analogues.

The presence of an *N*-hetero-atom produces a marked change in the interaction between the molecule and the solvent, compared with the hydrocarbon analogue. This interaction is responsible for the influence of the solvent

on the electronic spectra of N-heterocyclic compounds and sometimes produces a very marked change in the fluorescent properties. This influence has been described by Mataga and coworkers[15-17], Kasha[18,19], and Ermolaev and coworkers[20-22].

2. CHARACTERISTIC FEATURES OF BANDS DUE TO ELECTRONIC $n-\pi^*$ AND $\pi-\pi^*$ TRANSITIONS

Electronic absorption bands may differ in their position, intensity, behaviour in various solvents, and polarisation. In emission, electronic transitions may give fluorescence and phosphorescence bands differing in intensities (quantum yields), polarisation, behaviour in various solvents, lifetimes, or interval between the phosphorescence band and the fluorescence band or long-wave absorption edge when fluorescence is absent (this interval characterises the magnitude of the singlet-triplet splitting). Both absorption and emission electronic bands may also differ in vibrational structure and the degree of structure of the bands.

Kasha[1] was the first to formulate the characteristic empirical criteria of π, π^*- and n, π^*-bands; these were later refined and supplemented[18]. In a review devoted to the spectra of molecules with $n-\pi^*$ transitions (in particular the results of theoretical examination), Sidman[23] also gives a table of the characteristic features of $n-\pi^*$ and $\pi-\pi^*$ transitions.

It should be noted, however, that no one characteristic by itself is unambiguous, and the assignment of experimentally observed bands to a definite type of transition is possible only by examining all their characteristic features. If the molecule contains an electron-donating group of the type -OR, -SR, or $-NR_2$, the unshared pair of the hetero-atom of this group conjugates with the π-electrons, leading to marked changes in the electronic states and transitions[24,25]. We shall refer to these as $\pi, \pi^*(2p_z)$-states, to distinguish them from pure π, π^*-states. As far as luminescent properties are concerned, however, the levels of the π, π^*- and $\pi, \pi^*(2p_z)$-states are similar, so that for the sake of brevity we shall subsequently refer to them as π, π^*-levels.

The distinguishing characteristics of electronic bands of various types are summarised in Table 1.

Platt[26] examined theoretically the problem of the intensity of n, π^*-bands by analysing the local symmetry of the n, π^*-states, and showed that two types of transition are possible: those permitted and those forbidden by local symmetry.

If the n-orbital is a pure p-orbital, the transition is forbidden by local symmetry. If the n-orbital is a hybridised sp^2-orbital, the transition if permitted, and the intensity of the band is determined by the weight of the s-state:

$$\int n(1)\,\hat{M}\,\pi^*(1)\,d\tau \equiv \langle n(1)\,|\,\hat{M}\,|\,\pi^*(1)\rangle$$
$$\langle (s+p)\,|\,\hat{M}\,|\,\pi^*\rangle = \langle s\,|\,\hat{M}\,|\,\pi^*\rangle + \langle p\,|\,\hat{M}\,|\,\pi^*\rangle.$$

Thus the integral of the one-electron transition moment may be vanishingly small, even if the transition is permitted by the general molecular symmetry.

Calculations on the intensities of $n-\pi^*$ transitions were reviewed by Sidman[23] and Goodman[2].

TABLE 1. Characteristic distinguishing features of electronic bands of various types.

π,π^*-bands	$\pi,\pi^*(2p_z)$-bands	n,π^*-bands
Intensity of absorption bands		
Usually of high intensity (if not forbidden by symmetry) $\epsilon \geqslant 10^3$	Intense $\epsilon \geqslant 10^3$	Of low intensity even when transition permitted by symmetry ϵ from 1 to 10^3
Polarisation of absorption bands		
In the plane of the molecule	In the plane	Perpendicular to the plane of the molecule
Influence of polar solvent		
No change or slight displacement of the band, usually towards longer wavelengths	Marked displacement of band, usually towards longer wavelengths	Usually a short-wave displacement, to different extents for different molecules
Behaviour in acid medium		
Slight displacement, if molecule is preserved	Marked transformation	Disappears
Influence of electron-donating (conjugated) substituent		
$\pi,\pi^*(2p_z)$-bands appear in place of the π,π^*-bands. Occasionally some of the π,π^*-bands are preserved, but the band with longest wavelength is a new $\pi,\pi^*(2p_z)$-band		Band displaced towards shorter wavelengths
Fluorescence band		
Adjoins and partly overlaps the long-wave absorption band and is also polarised $\tau = 10^{-8}$–10^{-6} s	Highly sensitive to the nature of the solvent $\tau = 10^{-10}$–10^{-8} s	Either absent or of low intensity $\tau = 10^{-7}$–10^{-5} s
Phosphorescence band		
Long-lived phosphorescence with polarisation perpendicular to the plane of the molecule. Slight displacement in polar solvents τ = 0.1–10 s	Different displacements for different compounds τ = 0.1–10 s	Short-lived phosphorescence, often with high yield $\tau = 10^{-4}$–10^{-2} s
Magnitude of singlet-triplet interval		
Interval large (S^*,T splitting large) and dependent on the geometry of the π-system. For most known hydrocarbons it lies in the range 12 000–5000 cm^{-1}	Interval much smaller than that for the original hydrocarbon. Decrease greater, the stronger the electron-donating power of the substituent.	Interval relatively small (about 2000–3000 cm^{-1}) for molecules with one heteroatom (C=O, C=N, etc.). With several identical groups containing heteroatoms, the picture is complicated by splitting of the states, with removal of the degeneracy.
Sharpness of vibrational structure		
Diffuse vibrational structure for the vapour of most molecules studied. Often much sharper in frozen solutions, both for absorption and more particularly for luminescence.	Bands with diffuse structure predominate, both in the vapour and in solutions.	Exceptionally sharp structure in some instances in absorption and emission for the vapour. Absorption bands diffuse in solutions. Phosphorescence bands often show marked structure at low temperatures. The domination of the progression of an individual frequency is characteristic (for carbonyl compounds).

The difference in the magnitude of the S^*, T splitting for the n, π^*- and π, π^*-levels can also be explained. Examination of the dependence on structure of this splitting for π, π^*-levels in a series of aromatic hydrocarbons showed that its values lie in the range 12 000–4000 cm^{-1}. The magnitude of the S^*, T splitting for n, π^*-levels is always about 2000–3000 cm^{-1}. The magnitude of the S^*, T splitting depends on the magnitude of the two-electron exchange integral (between the orbital from which the electron is excited and the orbital into which it is transferred). For n, π^*-states it is determined by the integral $\langle n\pi^*\,|_G\,|\pi^* n\rangle$. This exchange integral is the energy of repulsion between two n, π^*-electrons and its value is small, since the functions of n- and π^*-orbitals are mutually orthogonal. The value of the integral will increase with increase in the overlap between the n- and π^*-orbitals.

The short-wave displacement of the n, π^* bands in polar solvents is attributed to binding of the n-electrons, leading to a decrease in the energy of the n-orbital. The binding is particularly effective when hydrogen bonds are formed. The binding of the n-electrons in acidic and alkaline media leads to disappearance of the n, π^*-bands.

The efficiency of fluorescence is limited by non-radiative processes. One of these is singlet-triplet conversion. Kasha attributed the luminescent characteristics of n, π^*-states to the high probability of singlet-triplet conversion. Clementi and Kasha[7] confirmed this theoretically by estimating the spin-orbital coupling in aza-heterocycles. Later, El-Sayed[8] showed that the magnitude of the spin-orbital coupling in aza-heterocycles between states with the same type of electronic configuration is of the same order of magnitude:

$$\frac{\langle S_{n\pi^*} | H_{s.o.} | T_{n\pi^*} \rangle}{\langle S_{\pi\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle} \sim 1$$

whereas between states with different electronic configuration it is greater by two to three orders of magnitude:

$$\frac{\langle S_{n\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle}{\langle S_{\pi\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle} \sim 10^2 - 10^3.$$

These results also explain the absence of fluorescence from n,π^*-levels in aromatic compounds, in which the $T_{\pi\pi^*}$-level usually lies between the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels, and also the absence of fluorescence from the $S_{\pi\pi^*}$-level, when the $T_{n\pi^*}$-level lies between this level and the $T_{\pi\pi^*}$-level.

The luminescent properties of molecules with n,π^*-levels should depend on the relative arrangement of the lower single and triplet levels of different character. There are five possible most characteristic mutual arrangements of excited singlet and triplet levels of the π, π^*- and n, π^*-type (Fig. 1). This classification was published earlier[27].

Type I. In molecules of this type the long-wave absorption band is due to an n–π^* transition and has a low intensity. In view of the relatively low probability of $S_{n\pi^*}$–$T_{n\pi^*}$ conversion, it is possible to have n, π^* fluorescence and weak short-lived n, π^* phosphorescence with a short interval (about 2000–3000 cm^{-1}) between the luminescence bands, or absence of luminescence, when non-radiative transitions have a high probability.

Type II. This corresponds to a long-wave absorption band of the n, π^* type, with low intensity. In these molecules there is a high probability of S^*–T conversion, responsible for extinction of the fluorescence. The spectrum shows a band due to short-lived n, π^* phosphorescence ($\tau \sim 10^{-4}$–10^{-2} s) in the frequency range 2000–3000 cm^{-1} below the long-wave absorption edge.

Type III. The lower triplet level is $T_{\pi\pi^*}$, and the lower singlet level $S_{n\pi^*}$. The weak long-wave n, π^* absorption band in these molecules is usually overlapped considerably by the stronger π, π^*-band and appears either as an inflection or as a weak long-wave "tail" (it is therefore difficult to observe experimentally). Fluorescence is also absent, since it is suppressed by $S_{n\pi^*}$–$T_{\pi\pi^*}$ conversion, for which the probability is high. The emission shows only long-lived phosphorescence, due to the $T_{\pi\pi^*}$–S_0 transition ($\tau \simeq 0.1$–10 s). The spectral interval between the long-wave absorption edge and the phosphorescence band will be greater than the first two types. The phosphorescence yield is expected to be lower than that for molecules of type II.

Type IV. This corresponds to a long-wave absorption band of the π, π^*-type, with high intensity. The luminescent properties of molecules of this type are similar to those of molecules of type III. A characteristic feature of these molecules is that direct experimental observation of the n–π^* transitions is difficult. The $T_{n\pi^*}$-level cannot be observed in emission, and the n, π^* absorption band is hidden by more intense bands. Thus the absence of fluorescence provides an important indirect criterion for estimating the energy of the $T_{n\pi^*}$-levels in molecules for which it is expected that this level lies between the $S_{\pi\pi^*}$- and $T_{\pi\pi^*}$-levels.

Since the excitation energy of the n, π^*-state is to a considerable extent localised on the bonds adjoining the hetero-atom, whereas for the π, π^*-state it is delocalised throughout the π-system, the $T_{n\pi^*}$–$T_{\pi\pi^*}$ conversion, according to Ermolaev and Terenin[28], is a process of intramolecular transfer of energy among triplet levels.

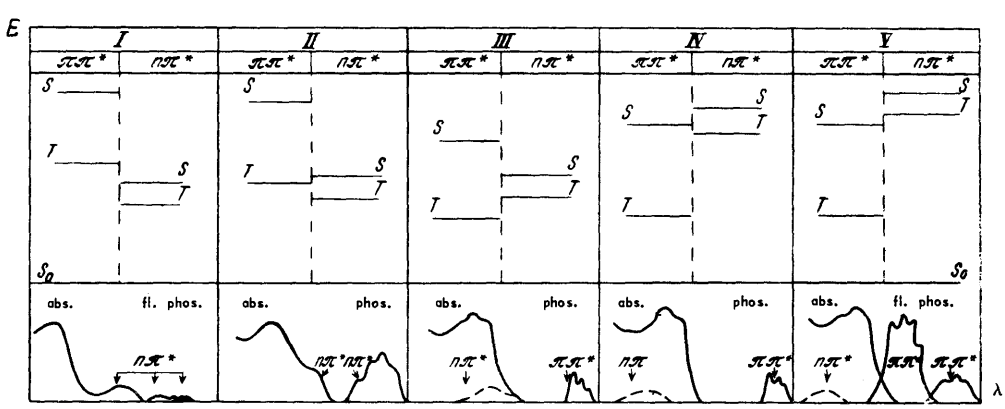


Fig. 1. Various types of arrangement of singlet and triplet π,π^*- and n,π^*-levels and the corresponding qualitative forms of electronic spectra.

Type V. Here the spectroscopic-luminescent properties are similar to those of the corresponding aromatic hydrocarbons. Both fluorescence bands and long-lived phosphorescence bands are observed.

Thus examination of the relative arrangement of the singlet and triplet n, π^*- and π, π^*-levels of molecules containing hetero-atoms and their assignment to one of the above types make it possible to understand the general character of the spectroscopic-luminescent properties of these molecules.

It should be noted, however, that this classification is not absolute, for the influence of various factors in a specific molecule may alter the ratio of the various transition probabilities and hence the luminescent properties.

Let us consider the various structural factors determining the mutual arrangement of the n, π^*- and π, π^*-levels. In systems with one hetero-atom, responsible for the $n-\pi^*$ transition, the energy of the $\pi-\pi^*$ transitions decreases more rapidly with increase in the π-system than the energy of the $n-\pi^*$ transitions. This is illustrated by the levels for the series: pyridine, quinoline, and acridine (Fig. 2). This relationship may provide an additional criterion for distinguishing n, π^*- and π, π^*-bands when the spectra of a series of compounds are compared.

When several identical hetero-atoms determining the n, π^*-levels are present, splitting of the n, π^*-levels takes place, so that the energy of the lower $n-\pi^*$-transition is reduced sharply. The magnitude of the splitting decreases rapidly with increase in the distance between the hetero-atoms. Thus in an aromatic hydrocarbon the replacement of several =CH– groups by an =N– atom leads to appreciable lowering of the $n-\pi^*$ transitions, whereas the $\pi-\pi^*$ transitions change little.

The splitting of the degenerate n, π^*-states in N-heterocycle was examined theoretically by El-Sayed and Robinson[29] on the basis of a localised model, in which it was assumed that the n-electron transferred to the π^*-orbital remains on the N atom, because of the coulombic attraction between this electron and the positive hole produced. El-Bayomi and Kearns[30] showed that the results of calculations based on a delocalised model provide a better explanation of the experimental data than do calculations based on a localised model. Both models predict an increase in splitting with decrease in the distance between the N atoms, and also a difference in the behaviour of the S^* and $T_{n\pi^*}$ states. Thus there should also be a change in the magnitude of the S^*, T interval for the lower n, π^*-levels.

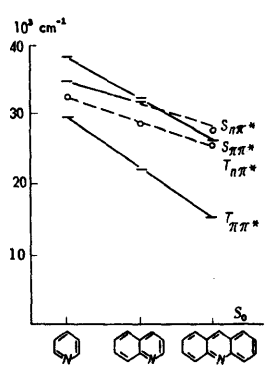


Fig. 2. Relative arrangement of the singlet and triplet π, π^*- and n, π^*-levels in the series: pyridine, quinoline, acridine.

The introduction of electron-donating substituents of the type –OR, –SR, and $-NR_2$ leads to a marked short-wave displacement of the n, π^*-bands (often by 2000–8000 cm^{-1}), whereas the π, π^*-bands are usually displaced towards longer wavelengths.

Finally, certain molecules, for example quinoline[8,18,19], show a change in the relative arrangement of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$-levels under the influence of solvent; this will be illustrated in more detail in Section 3.

3. CONDENSED AROMATIC HETEROCYCLES WITH ONE NITROGEN ATOM

Let us first consider the relationship between structure and the bands due to $n-\pi^*$ and $\pi-\pi^*$ transitions in the series pyridine, quinoline, isoquinoline, acridine, etc., that is, the hetero-analogues of the poly-acene series containing one N atom. The data are given in Table 2.

The n, π^* and π, π^* absorption bands of pyridine (I) were first identified by Kasha[1]. Rush and Sponer[31,50] described the absorption spectrum of pyridine vapour and carried out a vibrational analysis of the structure. In the vapour, the n, π^*-band of pyridine is resolved into a large number of sharp narrow bands with (0, 0)-band at 34 770 cm^{-1}, whereas the π, π^*-band consists of more diffuse bands (ν_{00} = 38 350 cm^{-1}). The intensity of the π, π^*-band ($\epsilon \sim 2000$) is slightly greater than that of the corresponding band of the transition in benzene, where it is forbidden by symmetry. The increase in intensity is related to the decreased symmetry of the pyridine molecule. According to Jaffé and Orchin[51], the fact that the intensity of the band is not as high as might have been expected for an allowed transition indicates that the departure of the distribution of the π-cloud in pyridine from D_{6h} symmetry is slight. Stephenson[52] used the absorption spectra of solutions to estimate the oscillator strengths of the $\pi-\pi^*$ transitions (f = 0.041 in 2,2,4-trimethylpentane) and the $n-\pi^*$ transition (f = 0.003). Kasha first assumed that the low intensity of the $n-\pi^*$ transition is due to the fact that it is forbidden by symmetry, but measurements in the vapour[50] did not confirm this assumption. The low f-value was attributed to the low value of the transition moment integral resulting from the small overlap of the ψ-functions of the ground and excited n, π^*-states[26]. Halverson and Hirt[32] studied the influence of solvents on the absorption spectrum and showed that in polar solvents the n, π^*-band (ν_{00} = 34 000 cm^{-1} in cyclohexane) undergoes short-wave displacement and is overlapped by the π, π^*-band, whose position does not change (ν_{00} = 38 000 cm^{-1}). On going from cyclohexane to alcohol, the displacement is about 2000 cm^{-1}.

The luminescence of pyridine could not be observed, although it might be expected to show phosphorescence of the benzene type[35]. The $T-S_0$ absorption spectrum[35] showed a band at 29 577 cm^{-1}, with frequency close to the frequency of the $T-S_0$ transition for benzene, so that it can reasonably be assigned to the $T_{\pi\pi^*}$-level. Theoretical estimation of the $T_{n\pi^*}$-level predicts a frequency of 32 000–33 000 cm^{-1}.

The absorption spectrum of quinoline (II) is similar to the spectrum of naphthalene (ν_{00} = 31 980 cm^{-1}) for the

TABLE 2. Frequencies of the electronic transitions (cm^{-1}) in *N*-heterocyclic aromatic compounds*.

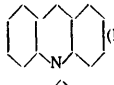
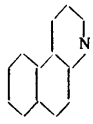
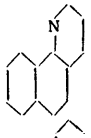
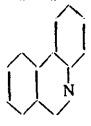
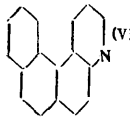
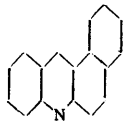
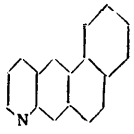
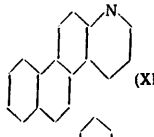
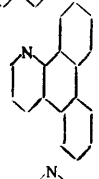
Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (I)	38 350 38 000	31 32	29 577	35	8 800	34 770 34 000 34 000	31 32 2	32000 29 600	35 2	2 000 4800
 (II)	32 000	13	21 800	11	10 200	32 000	15			2000—3000
 (III)	31 200	14	21 200	11	10 000					
 (IV)	25 300		15 840	36	9 460					
 (V)	29 000									
 (VI)	28 500	12 33	21 850	11 33	6 750					
 (VII)	28 700	12	22 050	12	6 650					
 (VIII)	25 650	34								
 (IX)	25 650	34								
 (X)	27 400	34								
 (XI)	29 000	34								
 (XII)	26 600	34								
 (XIII)	38 763	33				30 879 30 500 30 875 30 500 30 640	33 32 40 41	26 420 26 553 26 518	45 35 41	4459 3947 4357
 (XIV)	39 000	32				31 000 30 700 30 900	32 42 2	28 332 28 300	46 2	2668 2600
 (XV)	38 750	37				26 656 27 000 26 790	42 2	23 500	2	3290

TABLE 2 (contd.)

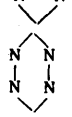
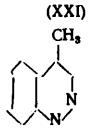
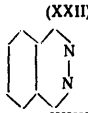
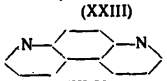
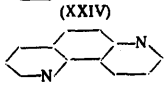
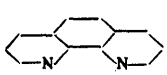
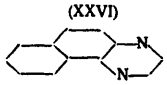
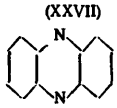
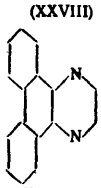
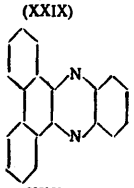
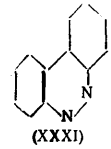
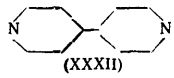
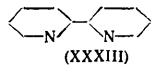
Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*_s T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*_s T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (XVI)	44 000	38				31 000 31 570	38 2	26 400 26 300	47 2	4600 5270
 (XVII)						17 970 18 135 17 800	5 43,44			
 (XVIII)			32 000	12						
 (XIX)	31 630	6,39	21 250	39	10 380	26 670	6			
 (XX)	32 200	39	21 900	39	10 300	27 330	6			
 (XXI)	31 980	39	21 800	39	10 180	25 820	6			
 (XXII)	31 000	39	19 000	39	12 000	23 050	39			
 (XXIII)	33 000	39	23 000	39	10 000	25 820	39			
 (XXIV)	29 800	12	22 200	12	7 600					
 (XXV)	29 700	12	22 150	12	7 550					
 (XXVI)	29 500	12	22 100 22 213	12 48	7 400					
 (XXVII)	27 500	38	21 000	38	6 500					
 (XXVIII)										
 (XXIX)	28 000		23 000		5 000					
 (XXX)	25 400	11	18 400	11	7 000					

TABLE 2 (contd.)

Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*, T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*, T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (XXXI)	28 000 28 800	48a				20 300 22 000	48a	13 500	48a	6 800
 (XXXII)	~34 000	49	24 530	49	9 470					
 (XXXIII)	~33 000	49	23 545	49	9 455					

* Several errors in the formulae have been corrected in the translation (Ed. of Translation).

long-wave π, π^*-band and does not contain a long-wave n, π^*-band. The long-wave absorption bands are classified as ^1L_b (32 000 cm^{-1}) and ^1L (35 000 cm^{-1}) according to Platt, and this is confirmed by polarisation measurements[13]. From the appearance, in the vapour, of exceptionally sharp $n-\pi^*$ absorption lines in the region of 3130 Å against a background of diffuse bands due to the $\pi-\pi^*$ transition, Mataga and coworkers[15] estimated the frequency of the $n-\pi^*$ transition is quinoline as 32 000 cm^{-1}. That this estimate is reasonable is also confirmed by the absence of fluorescence from quinoline in the vapour and hydrocarbon solutions[15-22]; the extinction of the fluorescence can be attributed to the fact that the $T_{n\pi^*}$ level lies slightly below the $S_{\pi\pi^*}$-level for quinoline. The frequency of the $T_{n\pi^*}-S_0$ transition can be estimated as 30 000 cm^{-1}, with the assumption that the magnitude of the S, T splitting of the n, π^*-level of quinoline is about 2000–3000 cm^{-1}, as in pyridine.

The appearance of a fluorescence band, similar to the band given by naphthalene, in polar solvents[15-22] is attributed to a change in the relative positions of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$-levels: under the influence of a polar solvent, particularly when intermolecular hydrogen bonding results, the energy of the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels is raised and they occupy a position above the $S_{\pi\pi^*}$-level of quinoline. Indirect confirmation that such an increase can occur is provided by the N-heterocycles with clearly defined n, π^*-bands, where these bands are displaced towards higher frequencies by 2000–3000 cm^{-1} on going from hydrocarbon solution to alcoholic solution.

Quinoline gives a long-lived phosphorescence band, whose position, structure, and polarisation are similar to those of the phosphorescence band of naphthalene[11]. Dorr and Gropper[11] showed that the phosphorescence spectrum at 90°K in alcohol consists of two series of bands. The frequencies of the main series of bands, with polarisation perpendicular to the plane of the molecule, are given by the formula $\nu = \nu_{00} - n\times1400$ cm^{-1}, where $\nu_{00} = 21\,800$ cm^{-1} and $n = 0, 1 \ldots 4$. The beginning of the secondary series is displaced by 500 cm^{-1} towards lower frequencies; this corresponds to the frequency of the asymmetric vibration, which alters by 90° the polarisation of the bands of this series relative to the main series.

The absorption[11], fluorescence, and luminescence spectra of isoquinoline (III) differ only slightly from those of quinoline.

The absorption spectrum of acridine (IV) is similar to that of anthracene. The fluorescence is weak in hydrocarbon solutions at room temperature, but it increases considerably in alcoholic solutions[15-17]. There is no information on the phosphorescence of acridine, but it is reasonable to expect it in the near infrared range, as for anthracene. Evans[36] reported $T-S_0$ absorption of acridine in the region of 15 800 cm^{-1}. The extinction of the fluorescence in hydrocarbons indicates that the $T_{n\pi^*}$-level in acridine is close to the $S_{\pi\pi^*}$ level, although slightly above it.

Spectroscopic data have been used to construct a scheme of triplet and singlet π, π^*- and n, π^*-levels for the series pyridine, quinoline, and acridine (Fig. 2); the change in the frequencies of the $\pi-\pi^*$ transitions in this series with increase in the π-system is the same as that in the polyacene series[10]. On linear ring addition, the frequencies of the $S_{\pi\pi^*}-S_0$ and $T_{\pi\pi^*}-S_0$ transitions decrease by 5000 cm^{-1} per benzene ring, whereas the magnitude of the S^*, T splitting of the π, π^*-level remains about 10 000 cm^{-1} (Table 2). The frequencies of the $n-\pi^*$ transitions decrease at less than half this rate. The decrease in the frequencies of the $n-\pi^*$ transitions is determined by the decrease in the energy of the π^*-orbital and provides evidence in support of the delocalised model of n, π^*-states in aza-heterocycles[30].

Since even in the quinoline molecule the energies of the $S_{\pi\pi^*}$- and $S_{n\pi^*}$-levels coincide and the n, π^*-band does not appear as a long-wave band, the band cannot be a long-wave band in more complex mono-aza-aromatic polycycles.

The absorption spectra of benzo[*f*]quinoline (V), benzo[*h*]quinoline (VI), and phenanthridine (VII) are similar to those of phenanthrene[34]. The introduction of the N atom into the phenanthrene ring leads to a slight displacement of the long-wave π, π^*-band and an increase in its intensity, The fluorescence spectrum ($\nu_{00} = 28\,500$) and phosphorescence spectrum ($\nu_{00} = 21\,850$ cm^{-1}) of benzo[*h*]quinoline in alcohol at 100°K [12,33] have discrete vibrational structure and are polarised, like the bands due to $S_1^*-S_0$ and $T-S_0$

transitions in phenanthrene. Analogous fluorescence (ν_{00} = 28700 cm^{-1}) and phosphorescence (ν_{00} = 22050 cm^{-1}) spectra were described for phenanthridine[12]. The frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions of the π,π^*-type for mono-aza-phenanthrenes differ from the frequencies for quinoline in approximately the same way as the frequencies of the phenanthrene transitions differ from the frequencies for naphthalene. They are also characterised by a decrease in the magnitude of the S^*, T splitting of the π,π^*-level to 6500–7000 cm^{-1}.

Similarity between the absorption spectra was established for the following pairs[34]: 1′-aza-3,4-benzophenanthrene (VIII)–3,4-benzophenanthrene; 3,4-benzacridine (IX)–1,2-benzanthracene; 5-aza-1,2-benzanthracene (X)–1,2-benzathracene; 3-aza-chrysene (XI)–chrysene; and 1-aza-triphenylene (XII)–triphenylene.

Thus in every instance the changes in the frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions of the π,π^*-type in catacondensed mono-aza-aromatic polycycles are analogous to those in the corresponding aromatic hydrocarbons[10].

From the established dependence of the frequencies of $\pi-\pi^*$ and $n-\pi^*$ transitions on the magnitude of the π-system of mono-aza-aromatic polycyclic compounds, it is not difficult to obtain a general picture of their spectroscopic-luminescent properties. These molecules have a low T-level of the π,π^*-type (beginning with pyridine) so that they can exhibit only long-lived π,π^*-phosphorescence. In the N-hetero-analogue of naphthalene—quinoline—the energies of the $S_{\pi\pi^*}$- and $S_{n\pi^*}$-levels coincide (in the vapour and hydrocarbon solvents) so that in compounds of this series (apart from pyridine) the n,π^*-band cannot appear as a long-wave band. In the acridine molecule, the energies of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$- levels coincide, so that those N-heterocycles (containing one N atom) whose $\pi-\pi^*$ transitions lie at shorter wavelengths than those of acridine will be non-fluorescent, whereas those whose $S_{\pi\pi^*}-S_0$ transitions lie at longer wavelengths will exhibit fluorescence like their hydrocarbon analogues. In acidic media and polar solvents, however, particularly when an intermolecular hydrogen bond is formed with the N atom, fluorescence may appear (be activated) for those molecules in which the $T_{n\pi^*}$-level lies above the $S_{\pi\pi^*}$-level. This is observed for quinoline, azaphenanthrenes, acridine, and benzacridine in alcoholic and other polar solutions.

4. AZABENZENES AND POLYCYCLIC COMPOUNDS WITH TWO OR MORE NITROGEN ATOMS

The introduction of two or more N atoms leads to more marked changes in the spectrum, influencing the positions and intensities of both the n,π^*- and π,π^*-bands. As a result of the interaction of the n,π^*-states of the N atoms, leading to splitting of the n,π^*-levels, the spectrum may show several n,π^*-bands. The interaction of n,π^*-states has been studied in most detail for the diazene series. It was established that the magnitude of the splitting depends to a marked extent on the mutual arrangement of the N atoms, decreasing rapidly with increase in the distance between them.

Azabenzenes

The spectra of diazines differ significantly from the spectra of pyridine and from one another.

Halverson and Hirt[33] found that the absorption spectrum of pyrazine (XIII) vapour consists of a system of sharp bands in the region of 3200 Å and a system of diffuse bands at 2800 Å, and assigned these to $n-\pi^*$ (ν_{00} = 30879) and $\pi-\pi^*$ (ν_{00} = 38763 cm^{-1}) transitions respectively.

The assignment of the bands was confirmed by a study of the behaviour of the absorption bands in various solvents[32]. In particular, a short-wave displacement of the n,π band was observed on going from cyclohexane to alcohol, although the displacement was much smaller ($\Delta\nu \simeq$ 300 cm^{-1}) than that for pyridine.

A detailed analysis of the vibrational structure of the long-wave absorption of the vapour enabled Japanese authors[40] to separate two overlapping systems of bands—a sharp system with a resolved 0–0 band equal to 30875 cm^{-1}, and a more diffuse system with lower intensity in the range 30500 cm^{-1}, assigned to a second $n-\pi^*$ transition, forbidden by symmetry. The behaviour of the absorption bands of pyrazine in various solutions was also described by Shimada[41], who also confirmed the $n-\pi^*$ character of the absorption band with ν_{00} = 30640 cm^{-1} in cyclohexane. Its frequency increases to 31020 cm^{-1} on mono-protonation, and the band disappears in solutions with salt formation[1]. The lower excited singlet level of pyrazine ($S_{n\pi}$) was assumed to be non-fluorescent[35]. Recently, Logan and Ross[53] reported the existence of two emission bands for pyrazine in the vapour and frozen hydrocarbon solutions. In the vapour, the band with shorter wavelength (in the region of 30000 cm^{-1}) adjoins the n,π^* absorption band, and the start of the long-wave band (at about 26500 cm^{-1}) coincides with the start of weak $T_{n\pi^*}-S_0$ absorption[45]. Innes and Giddings[45] obtained the rotational structure of the band due to the $n-\pi^*$ transition. In hydrocarbon solution at 80°K, pyrazine exhibits strong phosphorescence (with ν_{00} = 26420 cm^{-1}) and weak fluorescence with peaks at 29400, 28700, and 28050 cm^{-1}. Goodman and Kasha[35] studied the phosphorescence spectrum in an ether–isopentane–ethanol mixture at 90°K, and found that $\tau \simeq 0.02$ s and that the fluorescence band exhibits polarisation in the plane of the molecule. The influence of substituents, which led to short-wave displacement, confirmed the assignment of the phosphorescent T-level to the n,π^*-type.

Shimada[41] studied the phosphorescence spectrum of pyrazine in various media at 90°K and obtained good resolution of the vibrational structure, particularly in cyclohexane solution (ν_{00} = 26518–26445 cm^{-1}). It may be noted that in alcohol (ν_{00} = 26250) the fluorescence band does not show the characteristic short-wave displacement, indicating that this characteristic is not unambiguous. The $T-S_0$ transition was identified as an $n-\pi^*$ transition[41] from the behaviour of the phosphorescence band in acidic media, in which it undergoes appreciable extinction and is displaced towards higher frequencies, that is, it shows behaviour completely analogous to that of an n,π^* absorption band. Sidman[23] showed theoretically that the lower T-level is an n,π^*-level. The absorption in the region of the $T-S_0$ transition has also been described, with assignment to an 0–0 band equal to 26553 cm^{-1} in isopentane[35] or 26600 cm^{-1} in cyclohexane[37]. It has been shown theoretically[3] that the n,π^*-level lies at 31000 cm^{-1}. The dipole nature of the transition responsible for emission has been examined[54] and it was shown that the transition polarised in the plane of the molecule is symmetry allowed.

The absorption spectrum of pyrimidine (XIV) vapour, described by Uber and Winters[55,56], consists of a system of more than one hundred sharp narrow bands in the range

30 000–38 000 cm^{-1} and a system of broad diffuse bands in the range 39 000–45 000 cm^{-1}. From the behaviour of these bands in various solvents, Halverson and Hirt[32] assigned them to the $n-\pi^*$ transition (ν_{00} = 31 000 cm^{-1} in cyclohexane) and the $\pi-\pi^*$ transition respectively. Shimada[40] confirmed the assignment of the long-wave band to the $n-\pi^*$ transition, demonstrating that it disappears on salt formation.

It has been assumed that pyrimidine does not fluoresce from the n,π^*-state[18,19], but Börresen[57] had reported the observation of n,π^* fluorescence in liquid solution, and Goodman and coworkers[42] have described the n,π^* fluorescence spectrum at 298°K in 2,2,4-trimethylpentane (ν_{00} = 30 700 cm^{-1}) and found that $\tau = 10^{-9}$ s.

The phosphorescence band of pyrimidine—$\tau \simeq 10^{-2}$ s, ν_{00} = 28 332–28 218 cm^{-1} (cyclohexane), ν_{00} = 28 475 cm^{-1} (alcohol)—was studied in detail by Shimada[46], who obtained good resolution of the structure in various solvents. The phosphorescent level was interpreted as an n,π^*-level. In acid media the short-lived phosphorescence band disappears, with the production of weaker phosphorescence with $\tau \simeq 0.1$ s at shorter wavelengths, assigned to emission from the $T_{\pi\pi^*}$-level. The absorption spectrum of pyridazine (XV) vapour also shows two systems of bands—a diffuse system at 2500 Å and a sharp system with a purely electronic band at 26 656 cm^{-1} (3750 Å). According to Hirt[37], the long-wave band starting at 3700 Å in hexane is displaced towards shorter wavelengths by 300 Å in aqueous solution, whereas the second band—the π,π^*-band (2680 Å or 38 750 cm^{-1}) id displaced by only about 50 Å. Halverson and Hirt[32,33] assigned the first band to the $n-\pi^*$ transition, confirming this by observation of a short-wave displacement in polar solvents and under the influence of halogeno-substituents. Although Kasha assumes the existence of a $T-S_0$ transition of the $n-\pi^*$ type with energy 3.08 eV in pyridazine, Shimada[46] was unable to observe any luminescence, even at low temperatures. Goodman and coworkers[42] described the n,π^* fluorescence spectrum of pyridazine (ν_{00} = 27 000 cm^{-1}) in solution at 298°K with $\tau = 2.6 \times 10^{-9}$ s.

The absorption spectra of the vapour and solutions of *sym*-triazine (XVI) have been described[38]. The long-wave system of bands with initial band at 31 000 cm^{-1}, assigned to the $n-\pi^*$ transition on the basis of its behaviour in solutions, the influence of alkyl substituents, and the sharpness in the vapour, is more intense (ϵ = 880 at 36 780 cm^{-1}) than the diffuse system of bands due to the $\pi-\pi^*$ transition, starting at 44 000 cm^{-1} ($\epsilon \sim 150$ at 45 050 cm^{-1}). Paris and Hirt[47] described the phosphorescence spectrum of *sym*-triazine (ν_{00} = 26 400 cm^{-1} and τ = 0.44 s) and detected $T-S_0$ absorption. The $T-S_0$ transition was identified as an $n-\pi^*$ transition.

Mason[5] described the n,π^* absorption spectrum of *sym*-tetrazine (XVII) in the vapour and in cyclohexane solution at room temperature, and also in a mixture of hydrocarbons at 77°K (ν_{00} = 17 970 cm^{-1}). He obtained a resolved vibrational structure, particularly with the vapour (ν_{00} = 18 135 cm^{-1}). Chowdhury and Goodman[43,44] observed the n,π^* fluorescence of tetrazine with ν_{00} = 17 800 cm^{-1} and dimethyl-*sym*-tetrazine with ν_{00} = 17 100 cm^{-1} and $\tau \simeq 10^{-5}$ s. The existence of n,π^* fluorescence, observed for the first time for azines, is related to the absence of a $T_{\pi\pi^*}$-level between the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels, between which there is no direct spin-orbital coupling.

Thus the n,π^*-bands in diazines, triazine, and tetrazine lie at lower frequencies than those in pyridine, whereas their π,π^*-bands are approximately the same. The first theoretical examination of the spectra of azines was made by Orgel[58], who showed that the simple molecular orbital method, used to describe the orbitals of the ground state, is inadequate for a description of the excited states. The changes in the $n-\pi^*$ transitions and to some extent in the $\pi-\pi^*$ transitions were attributed to the electronegativity of the N atoms, leading to a lowering of all the n,π^*- and π,π^*-levels relative to the levels in pyridine. The greater changes in the frequencies of the $n-\pi^*$ transitions were related to the fact that two $n-\pi^*$ transitions are possible in diazines. Although these levels belong to different symmetry classes, there may be approximate degeneracy, because the overlap is small, so that the interaction between the atomic orbitals of the two atoms is small. This degeneracy is removed for excited n,π^*-states. Thus diazines are convenient materials for studying the interaction between excited chromophoric groups in n,π^*-states[29]. Splitting of the n,π^*-levels should lead to the appearance of two n,π^*-bands in the spectra. In accordance with this picture, detailed analysis of the spectra of pyrazine[40] and other diazines established two systems of bands due to $n-\pi^*$ transitions, one symmetry allowed and the other symmetry forbidden, as predicted by theory. The theoretical examination was carried out by Mason[3]. The relationship between the frequencies of the $n-\pi^*$-transitions in the diazone series has not been elucidated completely, however.

Diazanaphthalenes

Although the spectra of quinoline do not show the n,π^*-bands directly, and reveal only the $T_{n\pi^*}$-level in the extinction of the fluorescence, we may expect their appearance in diazanaphthalenes with the displacement of the $n-\pi^*$ transitions to lower frequencies as a result of splitting, as in the diazines. The spectra of the diazanaphthalenes differ significantly from one another. The chief difference is in the position of the n,π^*-bands. As already noted, the extent to which the frequency of the n,π^*-band is lowered increases with decrease in the distance between the N atoms.

The absorption spectra of 1,5-naphthyridine (XVIII) and 1,8-naphthyridine are similar to the spectrum of quinoline, and have n,π^*-bands at shorter wavelengths than the π,π^*-bands[6]. This is readily understood: the N atoms are fairly widely separated, and the effect of splitting is almost absent. 1,5-Naphthyridine apparently does not fluoresce in hydrocarbons but it exhibits fluorescence in alcohol and other polar solvents[12]. The long-lived phosphorescence band (ν_{00} = 22 000 cm^{-1}) is similar to the naphthalene band, but has less structure.

In quinoxaline (XIX), however, the n,π^*-band (26 670 cm^{-1}) appears as a long-wave band[6], and the π,π^*-band (31 630 cm^{-1}) coincides with the naphthalene band, like the prolonged phosphorescence band (21 250 cm^{-1}).

In quinazoline (XX) the n,π^*-band lies at even lower frequencies (27 330 cm^{-1}), and in phthalazine (XXIII) it lies at 25 820 cm^{-1},[6] whereas the π,π^* absorption and phosphorescence bands are similar to those of naphthalene, although the frequencies are slightly higher for phthalazine[39].

The electronic bands due to $\pi-\pi^*$ transitions in all the diazanaphthalenes are similar to the naphthalene bands; in particular, the characteristic magnitude of the S^*, T splitting of the π,π^*-level is preserved. The luminescent properties can be explained on the basis of the theories of

the n, π^*- and π, π^*-states, with allowance for the relative arrangement of their singlet and triplet levels.

Phthalazine has the most symmetrical molecule, and its spectrum is similar to that of naphthalene.

Cinnoline (XXI) gives three strong bands in the range 3100–3200 Å, whereas the other azanaphthalenes do not give bands in this range. The decrease in the energies of the $n-\pi^*$ transitions in diazanaphthalenes as the N atoms approach can be explained by arguments analogous to those for azabenzenes. As a result of this decrease, the long-wave absorption bands in the spectra of diazanaphthalenes are the n, π^*-bands, but the lower T-levels remain the $T_{\pi\pi^*}$-levels.

Diazaphenanthrenes

It is convenient to analyse the spectra of diazaphenanthrenes by comparing them with the spectra of phenanthrene. The absorption, fluorescence, and phosphorescence spectra of p-, m-, and o-phenanthrolines in alcohol solution are similar to the spectra of the original hydrocarbon, as already noted for the monoazaphenanthrenes. Thus the interaction of the n, π^*-states of the N atoms in the phenanthrolines does not produce such a marked decrease in the energy of the $n-\pi^*$ transitions, and they are found to be greater than the energy of the long-wave $\pi-\pi^*$ transition. The differences in the positions of the N atoms lead only to slight spectroscopic changes: the frequencies of the $\pi-\pi^*$ transitions are slightly higher for 4,7-phenanthroline (XXIV) ($S_1^*-S_0 = 29\,800$ cm^{-1}, $T-S_0 = 22\,200$ cm^{-1}) than for the 1,7-isomer (XXV) (29 700 cm^{-1} and 22 150 cm^{-1} respectively) and the 1,10-isomer (XXVI) (29 500 cm^{-1} and 22 100 cm^{-1})[12]. In the molecule of benzoquinoxaline (XXVII) the lower $S_1^*-S_0$ and $T-S_0$ transitions are also the $\pi-\pi^*$ transitions with lower frequencies (27 500 cm^{-1} and 21 000 cm^{-1} respectively in alcohol solution[38]). For diazaphenanthrenes, the magnitude of the S^*, T splitting of the π, π^*-levels remains at about 7500 cm^{-1}, as in phenanthrene; this is a characteristic feature of the geometry of a π-system with bent coupling of the rings[10]. The fluorescence of these compounds in alcoholic solutions is much weaker than that for phenanthrene, and is almost absent in hydrocarbon solvents; this can be attributed to the similarity in the energies of the $T_{n\pi^*}$- and $S_{\pi\pi^*}$-levels in these molecules.

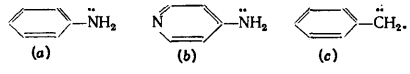
In the molecule of 9,10-diazaphenanthrene (benzocinnoline) (XXXI) with two neighbouring N atoms, the $n-\pi^*$ transitions lie at much longer wavelengths (the n, π^* absorption and fluorescence[48v] have $\nu_{00} = 20\,300$ cm^{-1}, and the n, π^* phosphorescence has $\nu_{00} = 13\,500$ cm^{-1}). Solutions of benzocinnoline give an n, π^* fluorescence band.

Other polycyclic aza-heterocycles whose spectra have been described include phenazine (XXVIII), dibenzoquinoxaline (XXIX), and dibenzo[a, c]phenazine (XXX); in the molecules of these compounds the N atoms are fairly far from one another, and the n, π^*-bands are masked by the π, π^*-bands, so that their spectra are similar to the spectra of the corresponding hydrocarbon analogues.

The spectra of bipyridyls do not show n, π^*-bands, and are similar to the spectra of biphenyl[49].

5. SUBSTITUTED N-HETEROCYCLIC COMPOUNDS

The introduction of substituents leads to various changes in both the absorption spectra and the luminescent properties. A particularly marked influence is shown by electron-donating substituents, which are so-called strong auxochromes. We shall not deal in detail with problems of the interpretation of the influence of substituents, and we refer the reader to the appropriate literature[24,25,59]. We would merely point out that substituents of the type NR_2, OR, and SR produce marked changes in the spectrum as a result of the conjugation of the electrons of the unshared pair with the π-electrons. A common feature of these substituted molecules is that the substituents increase the number of atomic orbitals by one unit and the number of π-electrons by two units. If the N-heterocycle forms an even alternant π-system, its derivative forms an odd alternant system, and this leads to the production of an upper filled π-orbital which is higher than that in the unsubstituted molecule. This is responsible for the appearance of an absorption band with longer wavelength and a decrease in the ionisation potential[59]. This can be illustrated more clearly by comparing the molecules of aniline (a) and aminopyridine (b) with the benzyl anion (c):



(a) (b) (c)

These systems are π-isoelectronic, and the benzyl anion has an upper filled π-orbital of non-bonding character[25].

Thus electron-donating substituents reduce the energy of the lower $\pi-\pi^*$ transitions. Experiment shows, however, that when these substituents are introduced the energy of the $n-\pi^*$ transitions is usually increased, so that these substituents displace the π, π^*- and n, π^*-bands in opposite directions. This characteristic feature of the behaviour of the bands with different character provides an additional criterion for their identification by studying the spectra of a series of substituted molecules.

The short-wave displacement of the n, π^*-bands can be explained qualitatively[39,58], by assuming that the substituents, by acting as electron donors, create a slight negative charge at the C atoms, which hinders the promotion of the n-electron of the N atom to the π^*-orbital. This transition requires even more energy, and the corresponding band lies at shorter wavelengths. A detailed semi-quantitative quantum-mechanical description of this displacement due to electron-donating substituents has not yet been made, however.

Different changes in the energies of the $\pi-\pi^*$ and $n-\pi^*$ transitions due to substituents may lead to changes in the relative positions of the singlet and triplet π, π^*- and n, π^*-levels, and hence in the luminescent properties of the molecules.

Let us examine spectroscopic data on the influence of substituents on the spectra of individual N-heterocyclic compounds.

Stephenson[52] studied the absorption spectra of the three isomers of picoline and 2- and 3-halogeno-substituted pyridines in a hydrocarbon solvent and in alcohol, and showed that in the 2- and 3-picolines, and also in the 3-fluoro, 3-chloro-, and 3-bromo-pyridines the n, π^*-band lies at the same position as that for pyridine, and is displaced in alcohol to higher frequencies by not less than 2000 cm^{-1}. In the spectrum of 4-picoline, the n, π^*-band is found at 35 200 cm^{-1}, but for 2-fluoro-, 2-chloro-, and 2-bromopyridines this band is hidden by the π, π^*-band. The spectra have been used to estimate the oscillator strengths of the $\pi-\pi^*$ and $n-\pi^*$ transitions. Rush and Sponer[50] published

the vibrational absorption spectra of picoline vapours (γ-picoline has $\nu_{n\pi^*} = 35\,165$ cm^{-1} and $\nu_{\pi\pi^*} = 38\,320$ cm^{-1}; for β-picoline the corresponding frequencies are 34 684 cm^{-1} and 37 380 cm^{-1}, and for α-picoline the corresponding frequencies are 34 753 cm^{-1} and 37 620 cm^{-1}). Misra[60] described the absorption spectra of 2-bromo- and 3-bromopyridine in all phase states, and also showed that the $n-\pi^*$ transition is observed for the 3-bromo-isomer ($\nu_{n\pi^*} = 35\,080$ cm^{-1}, $\nu_{\pi\pi^*} = 36\,300$ cm^{-1}) but is not observed for the 2-bromo-isomer; this is due to the inductive effect of the Br atom on the sp^2-electrons of the N atom.

The introduction of substituents of the type OR and NR_2 leads to more marked changes in the spectra; intense π, π^* absorption appears at longer wavelengths, whereas the n, π^*-bands cannot be distinguished. Mason[4] described the absorption spectra of hydroxy- and methoxypyridines in various media, put forward an interpretation of the bands, and discussed problems of tautomerism.

The presence of halogeno-substituents in pyrazine leads to a marked increase in the frequencies of the $n-\pi^*$ transitions. Halverson and Hirt[32] showed that the frequency is increased by 1700 cm^{-1} in 2-chloro-pyrazine and by 3200 cm^{-1} in 2,3-dichloropyrazine, relative to pyrazine. Hirt[37] described the $S_{n\pi^*}-S_0$ (32 068 cm^{-1}) and $T_{n\pi^*}-S_0$ absorption (28 100 cm^{-1}, $\epsilon \sim 0.05$) of pyrazine. The S_1^*, $T-n\pi^*$ splitting is about 4000 cm^{-1}.

Uber and Winters[55] described the absorption spectra of the vapours of dichloro-, trichloro-, and tetrachloropyrimidines, which have a system of bands with low intensity at long wavelengths, together with a more intense second system of bands. Halverson and Hirt[32] described the absorption spectra of chloropyridazine solutions. An n, π^* fluorescence band was observed for 3,6-dichloropyridazine[42]; the frequency of the 0–0 transition for this compound is higher than that for pyridazine, by 1800 cm^{-1}. Trimethyltriazine gives an absorption spectrum[38] with $\nu_{00} = 37\,880$ cm^{-1} for the $n-\pi^*$ transition and $\nu_{00} = 43\,960$ cm^{-1} for the $\pi-\pi^*$ transition, and also bands due to $T-S_0$ absorption and $T-S_0$ emission phosphorescence with $\tau = 0.65$ s), assigned to the $n-\pi^*$ transitions (ν_{00} for the $T_{n\pi^*}-S_0$ transition $\sim 27\,000$ cm^{-1}). Chowdhury and Goodman[44] studied the absorption spectrum and n, π^* fluorescence (with $\nu_{00} = 17\,000$ cm^{-1}) of dimethyltetrazine.

There are some unsystematic data on the spectra of substituted azanaphthalenes. The absorption spectrum of 4-methylquinoline at low temperature[61] and the spectra of dichloroquinazoline and 4-methylcinnoline [(XXII) (Ed. of Translation)][39] have been published.

Kosta and coworkers[62] studied the extinction of the fluorescence of dimethylquinoline solutions by halide, $C_6H_5NH_3^+$, SCN^-, and Cu^{2+} ions. Topolats and coworkers[63] described the extinction of the fluorescence of quinoline derivatives by gallic acid, hydroquinone, resorcinol, phloroglucinol, orcinol, and pyrocatechol. Witwer and Zanker[54] measured the polarisation absorption and fluorescence spectra of mono-and di-aminoacridines at low temperature.

Aromatic N-Oxides

The N-oxides are unique derivatives of aromatic N-heterocycles. Ziolkowsky and Dorr[64] studied the absorption, fluorescence, and phosphorescence spectra, and also the polarisation spectra, of the N-oxides of pyrazine, quinoline, 2-chloroquinoline, isoquinoline, and quinoxaline in various solvents at 90°K, and showed that the electronic absorption and luminescence bands are similar to the bands of the corresponding aromatic hydrocarbons and are very sensitive to change in the solvent; the spectra do not show n, π^*-bands. Thus the attachment of an O atom to the N atom in the hetero-ring leads to a marked change in the state of the n-electrons but has little influence on the π-system.

6. AZOMETHINES AND AZO-COMPOUNDS

A wide range of compounds of practical importance are included among the aromatic azomethines (A) and azo-compounds (B):



Ar—CH=N—Ar′ (A) Ar—N=N—Ar′ (B)

which formally have a π-system isoelectronic with the π-system of the corresponding arylethylenes. If the n-electrons of the N atom are localised on an atomic orbital, two types of transition are possible: $\pi-\pi^*$ and $n-\pi^*$; the π, π^*-bands can be expected to be similar to the bands for the corresponding arylethylenes. This is in fact observed for the molecules of azo-compounds with a planar structure, but is not observed for aromatic azomethines. The sharp difference between the absorption spectrum of benzylideneaniline and the spectrum of stilbene, and also a number of characteristic features of the absorption spectra of benzylideneaniline and its derivatives were attributed by Izmail'skii and Smirnov[65], and later by others[66,67], to the non-coplanar structure of these molecules. The conclusion that the benzylideneaniline molecule is not coplanar was confirmed by the quantum-chemical calculations of Minkin and coworkers[68,69]. The non-planar structure of benzylideneaniline is more stable than the planar structure because of the interaction of the unshared pair of electrons (the n-electrons) of the N atom with the π-electrons of the N-phenyl ring. This complicates the possibility of separating the electron transitions in benzylideneaniline into n, π^*- and π, π^*-types. Nevertheless, its long-wave absorption band has been assigned[66,70] to the $n-\pi^*$ transition.

Conjugation of the n-electrons and simultaneously a p-electron of the nitrogen atom with the π-electrons complicates considerably the interpretation of the spectra of molecules of type (A) with non-planar structure.

Let us consider the simpler case of planar molecules of type (A). The relative energies of the n, π^*-bands in a series of planar molecules (A) can be estimated by selecting a molecule with a shortened π-system. It is known that with increase in size of the π-system, the π, π^*-bands are displaced towards longer wavelengths much more rapidly than the n, π^*-bands, so that by shortening the π-system it is possible to achieve better separation of the π, π^*- and n, π^*-bands. In the absorption spectrum of N-benzylidenebenzylamine $C_6H_5CH{=}N{-}CH_2C_6H_5$, the n, π^*-band does not appear as a long-wave band (the estimated lower boundary $\nu_{n\pi^*} \geqslant 32\,000$ cm^{-1}). Thus the n, π^*-band cannot be the long-wave band in the spectrum of planar models of the molecules of benzylideneaniline $C_6H_5CH{=}N{-}C_6H_5$ and other aryl-substituted compounds with general formula (A), so that their spectra should be similar to the spectra of arylethylenes. This is in fact observed, when a planar structure is forced on molecules of type (A), for example, by enclosing the –CH=N– group in a benzoxazoline

ring. The spectroscopic-luminescent properties of arylbenzoxazoles and arylethylenes have been shown to be similar [65,72,73].

What then is the nature of the absorption spectrum of benzylideneaniline? It extends to much longer wavelengths than the spectrum of stilbene (Fig. 3). This displacement cannot be attributed merely to destruction of the coplanarity of the π-system, which should lead to a short-wave displacement. The benzylideneaniline molecule represents essentially a symbiosis of two molecules: aniline and nonplanar stilbene. Conjugation of the n-electrons with the π-electrons of the N-phenyl ring leads to the production of a system of "aniline" levels, whereas the participation of a p-electron of the N atom in π-conjugation defines a system of "stilbene" levels (Fig. 3). The chief factor [59] responsible for the long-wave displacement of the spectra of aromatic compounds when electron-donating substituents are introduced is the production of higher-lying upper-filled π-orbitals. Thus the long-wave absorption band of benzylideneaniline can be interpreted qualitatively by relating it to the transition of an electron from the upper filled "aniline" π-orbital to the lower vacant "stilbene" π-orbital. Since the electron of the "aniline" orbital is situated chiefly on the N atom and the probability of its transition is determined to a considerable extent by the overlap of the n- and p-orbitals of the N atom, which are mutually orthogonal, it is natural to expect that this transition will have a low probability, and this explains the low intensity of the long-wave band. The bands at shorter wavelengths probably result from the superposition of several transitions. It is reasonable to assume that the range 300–350 nm corresponds to superposition of the "aniline" and "stilbene" bands. Although quantum-chemical calculations have been carried out for the spectra of benzylideneaniline [67-69,74], a more rigorous and detailed theoretical examination of this unique molecule is desirable. The qualitative picture, which makes it possible to understand to some extent the differences between the spectra of benzylideneaniline and stilbene, can be extended to other aromatic azomethines whose spectra have been described [75].

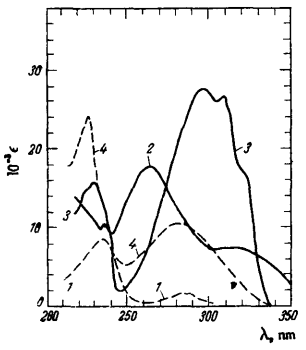


Fig. 3. Absorption spectra of aniline (1), benzylideneaniline (2), *trans*-stilbene (3), and *cis*-stilbene (4).

As expected, the absorption spectra of compounds of the type

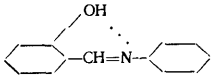
$$C_6H_5CH=N—C_6H_4—X—C_6H_4—CH=N—C_6H_5,$$

whose molecules consist of two benzylideneaniline molecules joined by a bridge X = $-CH_2-$ or $-CH_2-CH_2-$ which does not transmit π-conjugation, are similar to the spectra of benzylideneaniline [76]. The introduction of bridges X formed by –O–, –S–, or –NH– groups, which are electron donors, produces changes in the spectrum which are the same as the changes in the spectrum of benzylideneaniline resulting from the introduction of the substituents OH, SH, or NH_2 into the *para*-position of the aldehyde ring. The absorption spectra of compounds of this series were described by Krasovitskii and Mal'tseva [77]. Increase in the number of benzene rings between the azomethine groups in $C_6H_5CH=N-(C_6H_4)_n-N=CH-C_6H_5$ from $n = 1$ to $n = 3$ does not alter the absorption spectrum [76].

Azomethine compounds of the above types do not show luminescence. The absence of luminescence is apparently due to the non-coplanar structure, which is characterised by an extinguishing effect resulting from the excitation of torsional vibrations.

The introduction of substituents leads to complicated changes in the electronic structure of the molecules, and also influences their degree of non-coplanarity. This complicates the spectra and may alter the luminescent properties of the molecules. The interpretation of the spectra of these derivatives is very difficult. It is clear, however, that the introduction of substituents cannot lead to the appearance of $n-\pi^*$ transitions as long-wave transitions.

With Kozlov, Shigorin, and Puchkov [78-80], we showed that a particularly marked change in spectroscopic-luminescent properties is produced by the introduction of an OH substituent into the *o*-position of the aldehyde ring. *o*-Hydroxybenzylideneaniline (I)

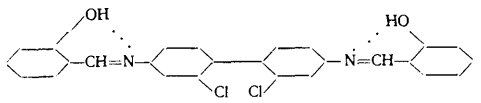


(I)

exhibits bright green fluorescence at 77°K and reversible phototropic properties. The absorption spectrum of *o*-hydroxybenzylideneaniline contains a weak long-wave band, previously assumed to be the n, π^*-band. This band shows an anomalous increase in intensity on going from a non-polar solvent to a polar solvent [81]. Studies of the spectra of *o*-hydroxybenzylideneaniline under various conditions and of the phenomenon of phototropy established [79,80,82] that the long-wave band belongs to another tautomeric form of the *o*-hydroxybenzylideneaniline molecule, whose relative concentration depends on the nature of the solvent and temperature. No explanation has yet been given, however, for the anomalously large Stokes displacement between the long-wave absorption and the fluorescence band [82,83].

The absorption and luminescence spectra of various hydroxyazomethine compounds have been studied [84]. It was shown that doubling of the *o*-hydroxybenzylideneaniline molecule displaces the intense band by about 2500 cm^{-1}, that is, the displacement is not as great as that observed on going from stilbene to bistilbene, and the displacement of the long-wave band (assigned to the other form) is even smaller. A remarkable feature is that the absorption spectrum does not depend on the number of phenyl rings

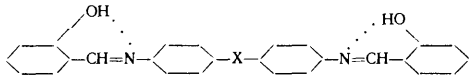
between the N atoms, although there is undoubtedly a conjugation effect, as indicated by the short-wave displacement of the band for (II):



(II)

compared with the molecule which does not contain substituents causing steric hindrance.

It was also shown[77] that the bridge X = –O–, –S–, or –NH– in the molecules (III):



(III)

influences the spectra as an electron-donating substituent, but it does not exhibit the properties of a conjugation transmitter.

Arylazo-Compounds Ar–N=N–Ar′

These have molecules with planar structures. Their intense absorption bands, due to $\pi-\pi^*$ transitions, are similar to the bands of the corresponding arylethylenes[75,85] and the long-wave range (20 000–24 000 cm^{-1}) shows a weak band due to the $n-\pi^*$ transition, which has been most extensively studied for azobenzene. Jaffé and coworkers[70] carried out a detailed study and theoretical examination of the spectra of azobenzene and related compounds. On the basis of the small short-wave displacement in polar solvents and under the influence of substituents, they assigned the long-wave band at 420 nm to an $n-\pi^*$ transition, assuming that it is formed by the superposition of two bands due to $n_a-\pi^*$ and $n_s-\pi^*$ transitions. It should be noted, however, that their method of graphical resolution of the bands has no real basis and can hardly be correct. Dyck and McClure[86] described the structure of the band due to the $\pi-\pi^*$ transition (ν_{00} = 27 662 cm^{-1}), resolved in a mixed azobenzene–bibenzyl crystal at 20°K, using the frequencies 220, 378, and 1342 cm^{-1}. The last frequency was assigned to the stretching vibration of the –N=N– group in the excited π, π^*-state. Hochstrasser and Lower[87] showed that the n, π^*-band exhibits polarisation in the plane of the molecule and that the transition is forbidden by symmetry, in agreement with theoretical calculations of the splitting of the n, π^*-states of the two nitrogen atoms. The magnitude of the splitting was estimated as 8900 cm^{-1}. This estimate agrees with experiment. As noted above, for one N atom the band due to the $n-\pi^*$ transition is expected in the region of 32 000 cm^{-1} (planar benzylideneaniline model) and for azobenzene the $n-\pi^*$ transition lies at about 22 000 cm^{-1}. The molecules of arylazo-compounds may exhibit two configurations: *cis* and *trans*[75,85,86]. The *trans*-configuration is the more stable. The absorption spectra of the *trans*-isomers of various arylazo-compounds Ar–N=N–Ar′ (where Ar = phenyl, α-naphthyl, or β-naphthyl) have been described[85]. The *trans*-isomers may be converted into the *cis*-isomers under the influence of light. The study of the photo-*trans*-*cis*-isomerisation of azo-compounds has been the subject of a number of papers[88]. The spectra of the pure form of *cis*-azobenzene have been isolated and studied[89], and the absorption spectra of the *cis*-isomers of more complex azo-compounds have been described[90,91].

Azo-compounds form one of the most extensive classes of non-fluorescent compound. The absence of fluorescence is apparently due to the high probability of S^*-T conversion from a lower $S_{n\pi^*}$-state into the $T_{\pi\pi^*}$-state, and is also related to the photochemical instability of azo-compounds.

Derivatives of azo-compounds form a large class of organic dyes, so that a large number of their spectra have been studied. Brode and Wyman and coworkers[92–96] studied the absorption spectra of a large number of azo-compounds and azo-dyes in order to establish the relationship between the spectra and chemical structures of the dyes. The phenomenon of phototropy and the *cis*-*trans*-isomerisation of aromatic azo-compounds have been described[92], and the influence of dissolution and temperature on the *cis*-*trans*-isomerisation of the amino-, hydroxy-, alkyl-, and halogeno-derivatives of azobenzene, benzeneazonaphthol, and benzeneazonaphthylamine has been described[51]. The appearance of a new absorption band in the spectrum of azo-dyes as a result of the hydration of the dye molecules when water is added to the organic solvent has been described[94]. The change in the spectra accompanying the interaction of the molecules of binary mixtures of dyes in aqueous solutions[95] and the phenomenon of phototropy in solutions of complex diazo methoxyazo-dyes[96] have also been studied.

A series of papers by Heilbronner, Gerson, Schulze, and coworkers[75,97–106] described the study of the electronic structure and properties of azo-compounds. The ultraviolet absorption spectra of arylazoazulenes have been studied[97,98] and it has been established that the displacement of the band shows a simple dependence on the Hammett constant; the dipole moments of phenylazoazulene derivatives have been studied[99] and the spatial structure of the molecules has been established. The π-electronic structure of phenylazoazulene has been examined theoretically by the MO LCAO method[100], and the energies of transitions and the oscillator strengths have been calculated. A special study has been made[101] of the problem of the influence of a substituent in the benzene ring on the position of the absorption band in the range 16 500–17 000 cm^{-1}, and a study has been made[41] of the bathochromic shifts of the bands accompanying the protonation of the molecules of arylazoazulene derivatives in ethanol–hydrochloric acid systems. Study of the spectra of *trans*- and *cis*-azobenzenes[103] in acid solutions showed that their conjugate acids have different structures; the *cis*-isomer of the acid is gradually converted into the *trans*-form. The spectra and structure of the *p*,*p*′-bis(dimethylamino)azobenzene azonium cation have been studied[105] and the influence of protonation on the spectra of *p*′- and *m*′-derivatives of *p*-dimethylaminoazobenzene[97,98] *p*-dimethylaminophenylazoazulenes[106] has been described.

Robin and Simpson[107] studied the absorption spectra of polyphenyl azo-dyes $C_6H_5-N=N-(C_6H_4-N=N-)_n-C_6H_5$ (n = 0–5); the spectra were interpreted on the basis of a model with transfer of the electronic excitation along the chain of the molecule, the polarisation of the transitions was established, and the $n-\pi^*$ transitions were isolated.

Skulski and Urbanski described the absorption spectra of azo-dyes based on 4-hydroxy- and 4-acetoxyazobenzenes[108], 4-formyl-, 4-nitro-, and 4-(2-nitrovinyl)azobenzenes[109], and acetoxy- and acetylamino-derivatives of 1-phenylazonaphthalene[110]. It has been established[108] that electron-accepting groups in the *o*-position relative to the phenol groups in the dyes $X-C_6H_4-N=N-C_6H_3YOH$ produce a hypsochromic shift of the adsorption band. The absorp-

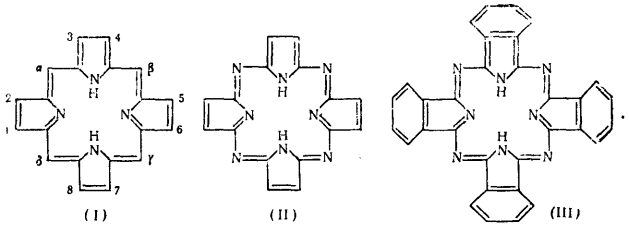
spectra of *o*- and *p*-azo-dyes based on 1-phenylazonaphthalene have also been described[111,112].

Si-Jung and Jaffé[113] studied the transfer of the electronic effects of the $-N=NC_6H_4-$ group in the compounds p-$HO-C_6H_4N=NC_6H_4-X$, where X = OCH_3, CH_3, or Br. Baba[114] studied the influence of intermolecular hydrogen bonding on the absorption spectrum of *p*-hydroxyazobenzene, and showed that the n, π^*-band is displaced towards shorter wavelengths, and the π, π^*-band towards longer wavelengths. It was shown that the displacement of the frequencies is greater for the O–H...N < bond than for the O–H...O < bond.

It is pointed out in Pringsheim's monograph[115] that among more than 700 azo-dyes there is no example of fluorescence in solutions. With Shigorin, Kozlov, and Puchkov[116,117], we investigated structural factors leading to activation of the fluorescence of azo-compounds, and showed that this activation is facilitated by the introduction of an *o*-hydroxy-substituent, which leads to the formation of an intramolecular six-membered quasi-aromatic ring with hydrogen-bonding, and that this ring stabilises the structure of the molecule. The *o*-hydroxyazo-compounds exhibit bright fluorescence in powders and frozen solutions. The substance becomes non-fluorescent when the OH group is methylated. The fluorescent S_1^*-state in the *o*-hydroxyazo-compounds is the π, π^*-state. It is lower because of the decrease in frequency caused by the electron-donating OH substituent, whereas the OH...N interaction removes the degeneracy of the n, π^*-states (the N atoms are not equivalent) and leads to marked displacement of the frequency of the $n-\pi^*$ transition towards higher values.

7. PORPHYRINS AND PHTHALOCYANINES

Without examining in detail the relationship between the spectra and structures of the molecules of porphyrins and phthalocyanines (although this problem deserves attention, despite the existence of a number of reviews[118-120] and theoretical calculations[121-123]) let us examine the extent to which the spectra of these complex systems show general regular features characteristic of heterocyclic compounds. It is of interest to determine the range of the spectrum in which we can expect $n-\pi^*$ transitions for these molecules and to find whether they exhibit luminescence.



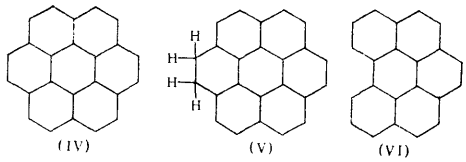
(I) (II) (III)

Porphine (I), the parent compound of the porphyrins, has a lower $S_1^*-S_0$ transition in the region of 6130 Å (16 300 cm^{-1}), active in absorption and fluorescence. Solov'ev, Sevchenko, and coworkers[124] obtained a quasi-line multiplet structure for the fluorescence and absorption bands of porphine in octane at 77°K. There is no information on the phosphorescence of porphine. To understand the relationship between the spectrum and the structure, let us consider the characteristic features of the structure of the porphine molecule. Formally, it is obtained by forming a ring of four pyrrole groups by means of methine bridges. In the process, only two pyrrole rings are preserved; the N atoms of these rings each bring one atomic orbital and two electrons into the π-system. The N atoms of the other two rings each bring one atomic orbital and one electron, and also carry n-electrons, capable of giving $n-\pi^*$ transitions. These could be the lowest frequency transitions, as with the previously examined *N*-heterocycles, only if the entire absorption spectrum lay above 32 000 cm^{-1}. Since the absorption of porphine begins at much lower frequencies, due to the extensive π-system, the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels in molecules of this type will lie above the $S_{\pi\pi^*_n}$-level and will not influence the luminescence of the molecules. The cyclisation of four pyrrole rings to give one large ring should produce properties characteristic of the angular cyclisation of aromatic nuclei. It is convenient to compare the skeletons of porphine and coronene (IV), whose outer perimeters have approximately the same number of π-electrons. As already noted, on angular cyclisation the long-wave bands are α-bands of low intensity (in coronene this band is further forbidden by symmetry). The greater lowering of the frequency of the $S_1^*-S_0$ transition in porphine compared with coronene is due to the presence of the NH group, which produces the strong bathochromic shift of the bands, discussed in Section 5. The angular cyclisation itself does not lead to marked lowering of the frequency of the $\pi-\pi^*$ transition. This is effectively confirmed for porphyrins on going from porphine to tetrabenzoporphyrin, which gives a frequency in the region of 15 200 cm^{-1}, that is, only 1100 cm^{-1} below the $\nu_{S_1^*-S_0}$ frequency of porphine (or only 270 cm^{-1}, calculated for one benzene ring). Shkirman and Solov'ev[125] also obtained a quasi-line structure for the fluorescence and absorption bands of tetrabenzoporphine in octane at 77°K. An important characteristic feature of angular cyclisation is the decrease in the magnitude of the S^*, T splitting, which can also be expected for porphine. Although phosphorescence is not known for porphine, its T-level can be determined from data on metalloporphyrins. The intrdouction of a metal, producing little change in the frequency of the $S_1^*-S_0$ transition, leads to an increase in the relative phosphorescence yield with increased atomic weight of the metal. In various metallomesoporphyrins, the magnitude of the S^*, T splitting is about 3000–3500 cm^{-1},[126] which is even slightly less than that in coronene. It is reasonable to attribute the additional decrease to the electron-donating effect of the NH and N–metal groups. Thus it is also possible, for the complex porphyrin molecules, to distinguish those characteristic features of the spectra which are determined by the topology of their π-electronic structure or the topology of the molecular framework over which the π-electrons are distributed.

This conclusion is further confirmed by examining molecules which are related to porphine but which have a smaller π-system, and this in turn makes it possible to understand various spectroscopic-luminescent characteristics of these molecules.

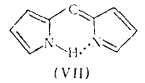
In the molecule of chlorin (which differs from porphine in that it contains a hydrogenated 1–2 bond), the frequency of the $S_1^*-S_0$ transition is displaced towards lower frequencies (ν_{00} = 15 780 cm^{-1})[125]. Rabinowitch tried to attribute this displacement and the increase in the intensity of the long-wave absorption band to the production of a new lower-lying excited level; the band associated with transition to this level is assumed to mask the "porphine" bands of low intensity. It is not at all clear how decrease in the π-system leads to an increase in the number of electron

levels (preservation of the former levels and the production of a new level). Sevchenko and coworkers[124] consider than this explanation is without foundation, but they in turn assume a correlation between the levels of chlorin and porphine. It is not rational, however, to look for such a correlation. When one double bond is eliminated in the coronene ring:



(IV) (V) (VI)

there is also a long-wave displacement of the $\pi-\pi^*$ transition. The spectroscopic properties of dihydrocoronene (V) are similar to those of 1,12-benzoperylene (VI), whose molecule can reasonably be regarded as a doubled phenanthrene molecule[10]. Thus the hydrogenated bond in the chlorin molecule produces the long-wave displacement as a result of the sharp decrease in the circular symmetry, that is, the change in the topology of the π-system. This also explains the difference in the intensity of the band and the absence of phosphorescence. The magnitude of the S^*, T-splitting in 1,12-benzoperylene is approximately double that in coronene. If this also applies on going from porphine to chlorin, the frequency of the $T-S_0$ transition of the latter will lie in the region of 10 000 cm^{-1}. The probability of $T-S_0$ emission in this range would be expected to be very low, because of the strong non-radiative deactivation. This is apparently related to the absence of phosphorescence in metallochlorins[127], although metals such as Cu have a marked ability to increase the phosphorescence yield. Increase in the magnitude of the S^*, T splitting (up to 7000 cm^{-1}) takes place in the molecule of bipyrrole (VII), which is as it were half a porphine molecule:



(VII)

The absorption band for this compound lies in the region of 20 000 cm^{-1}, that is, 3700 cm^{-1} higher than that for porphine. However, the displacement is very slight in relation to the position of the pyrrole band at about 220 nm.

Although bipyrrole exhibits fluorescence, replacement of the methine group by –N= leads to extinction of the fluorescence. The extinction is apparently due to the fact that the π-electrons of the pyrrole ring are conjugated with the n-electrons of the N atom. This leads to breakdown of the planar structure of the π-system, as in benzylideneaniline.

In tetra-azaporphine (II), the =CH– methine bridges are replaced by =N–. This replacement produces almost no displacement of the π, π^*-band (16 350 cm^{-1})[125]. In phthalocyanine (tetrabenzotetra-azoporphine) (III), the frequency is lowered by only 1900 cm^{-1} relative to that for tetra-azaporphine[128].

Evstigneev and coworkers[129-131] and Livingston, and coworkers[132,133] observed "activation" of the fluorescence of chlorophyll: the absence of fluorescence in non-polar solvents and the production of fluorescence when polar solvents were added. The first authors[129-131] attribute this "activation" to breakdown of chlorophyll associates, whereas the second authors[132-135] attribute it, by analogy with quinoline, to a change in the relative position of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$-levels under the influence of the polar solvent. Simple analysis of the structural characteristics of the chlorophyll molecules shows, however, that the $n-\pi^*$ transitions in these molecules cannot be as low as this. In actual fact, as noted for porphine, the energy of the n, π^*-levels in this molecule is much greater than that of the π, π^*-levels. The same is true for tetra-azaporphyrin, since increase in the number of N atoms cannot lower the n, π^*-levels because of their splitting; the latter should be small, because of the relatively short distance between the N atoms. The presence of C=O groups in the chlorophyll molecule may lead to the appearance of n, π^*-bands in the range 27 000–26 000 cm^{-1}, that is, again at higher frequencies than the lower π, π^* transitions of the π-system of the porphine ring. This provides further confirmation of the interpretation given by Evstigneev and coworkers[129-131].

In conclusion it may be noted that the above general features, relating the spectra to the molecular structure, make it possible to obtain an overall picture of the spectroscopic-luminescent properties of a wide range of organic compounds. Many of these regular features require theoretical examination.

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NOTE ADDED IN PROOF

The following reviews appeared after the present paper had been submitted for publication: one by Lower and El-Sayed[136], devoted to the triplet state in intramolecular electronic processes, one by Innes[137] on the spectroscopic properties and geometry of the excited electronic states in azines, and their theoretical interpretation, and a Russian translation[138] of Mason's review on the electronic absorption spectra of heterocyclic compounds.

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ALKALI METAL FLUOROHALOGENATES

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I. INTRODUCTION

Compounds of fluorine with all the elements are known. Until recently the noble gases constituted an exception, but advances in the chemistry of inorganic fluorides in recent years led to the synthesis of the fluorides of these elements too in a pure state [1,2]. The interest in fluorine is largely due to its unusual "extreme" position in the Periodic System—its unusual chemical reactivity. The extremely high oxidising power of fluorine led to its wide application in the preparation of compounds of many elements in their highest valence states [3-7]. These compounds are in turn important in practice, being used in many branches of the new engineering, in the first place in the technology of the processing of nuclear fuel [8-10].

Certain highest fluorides, which are solids, are also powerful fluorinating agents, but considerably inferior to elemental fluorine. As an example, one may mention the difluorides of silver and mercury [11-13], the trifluorides of cobalt and manganese [11, 14-16], lead tetrafluoride [17], and others [18-22].

The compounds of fluorine with the other halogens constitute the most interesting class of inorganic fluorides because they are unusual and highly reactive compounds. They can be synthesised relatively easily, many of them are liquids under normal conditions, and they all behave as very powerful fluorinating agents. Halogen fluorides can be arranged in the following series in terms of their reactivity:

$$ClF_5 > ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > IF_3 > IF$$

The reactivity of chlorine trifluoride approaches almost that of elemental fluorine, and with certain inorganic and organic substances ClF_3 actually reacts more vigorously [23]. For example, even before the discovery of halogen fluorides, it was noted that the addition of small amounts of chlorine to fluorine enhances the activity of the latter [24]. There is no doubt that this is associated with the formation of chlorine fluorides.

Chlorine pentafluoride ClF_5 was not obtained in a pure form until 1966, [25] its chemical properties have not been investigated, and, in view of the lack of experimental data, its oxidising power can only be inferred from general relations governing the activity series of halogen fluorides. However, it is quite evident that ClF_5 is a most powerful oxidising agent and an extremely active fluorinating agent, approaching elemental fluorine in these properties.

Chlorine trifluoride, like fluorine itself, can oxidise many metals to their highest valence, but it has an important advantage over elemental fluorine in that it is easy to

handle, can be relatively readily stored, can be transported, and can be used in the liquid state. Chlorine trifluoride converts silver chloride and fluoride into the difluoride and cobalt difluoride into the trifluoride[26,27], and as mentioned above, these compounds are some of the most powerful solid fluorinating agents used. Not only many transition metals, but also oxides are fully converted into the highest fluoride when acted upon by chlorine or bromine trifluoride[28-32].

The above remarks account for the great interest in the chemistry of halogen fluorides. The methods for their synthesis and their physical and chemical properties are being investigated very vigorously and a number of extensive reviews have been published on these topics[20-23,33-37]. There is no doubt that inorganic fluorides, which may be somewhat inferior in their oxidising power to elemental fluorine and halogen fluorides but are solid under normal conditions, are of great practical interest and can find wide application as powerful fluorinating agents. From this point of view, alkali metal fluorohalogenates, the most active of which have been synthesised literally in the last 2–3 years and whose chemistry has developed enormously at the present time, are the most promising.

Table 1 lists all the alkali metal fluorohalogenates known at present and includes for comparison the data for halogen fluorides and elemental fluorine. It is noteworthy that alkali metal fluorofluorates, i.e. compounds of the type $M[F(F_2)]$, where M is an alkali metal, would be most promising from the point of view of their employment as highly active fluorinating agents, but repeated attempts to synthesise such compounds have been unsuccessful so far[38-45]. Nevertheless, similar compounds of chlorine, bromine, and iodine are known, have been isolated in a pure state, and have been investigated in fair detail; their stability increases in the series Cl–Br–I.[46-50]

Evidently the analogous fluorine compounds also exist but, in conformity with the general tendency of halogens, alkali metal fluorofluorates must be very unstable; in all probability this is why their synthesis and isolation present considerable experimental difficulties, which unfortunately have not been overcome as yet.

The advantages of alkali metal fluorohalogenates as fluorinating agents are as follows: (a) high oxidising power of the compounds, greatly exceeding that of all known solid fluorinating agents; (b) the possibility of carrying out reactions at elevated temperatures without the development of a high pressure in a closed system, which means that fluorination can be performed in relatively simple apparatus; (c) the use of purer fluorinating agents than is the case when elemental fluorine or halogen fluoride are used for this purpose; (d) ease of handling of the solid substances; (e) the achievement of complete fluorination (by virtue of the higher temperatures used) of the compounds for which this is impossible in the presence of halogen fluorides, for example.

The last finding is confirmed by the data of Table 2, where compounds which are only partially fluorinated by bromine trifluoride even under severe conditions are listed. On the other hand, when potassium tetrafluorobromate(III) $KBrF_4$ is used, the reaction goes to completion after a relatively short time[51].

Apart from the possibility of using alkali metal fluorohalogenates as fluorinating agents, it is interesting to note that their application for analytical purposes to determine oxygen, and also in isotopic geology, for the removal of oxygen from minerals[51], is also promising.

Alkali metal fluorohalogenates are not only of great practical value but they also constitute a class of inorganic compounds which is of considerable theoretical interest. It has been established[52,53] that halogen fluorides are ionisable solvents, which dissociate according to the equation

$$2XF_n \rightleftarrows XF^+_{n-1} + XF^-_{n+1}.$$

Consequently these substances are amphoteric solvents and their behaviour can be most readily understood on the basis of the acid–base theory of non-aqueous solvents[33,52-59]. The fluoride ion plays a role analogous to that of the proton, namely the addition of a fluoride ion is equivalent to the loss of a proton [sic (Ed. of Translation)].

TABLE 1. Conditions of synthesis and certain physical properties of alkali metal fluorohalogenates, halogen fluorides, and elemental fluorine.

Compound	Fluorine content, wt. %	Synthetic reaction	Temperature of synthesis, °C	M.p., °C	Decomposition temperature, °C
$NaClF_2$	39.38	$NaF+NOClF_2=NaClF_2(?)+NOF$	150	—	—
$KClF_2$	33.75	$MF+NOClF_2=MClF_2+NOF$	150	—	237
$RbClF_2$	23.90	or	25—230	—	248
$CsClF_2$	18.41	$MF+ClF=MClF_2$	175	—	262
$KClF_4$	50.46	$MF+ClF_3=MClF_4$	100	—	~200
$RbClF_4$	38.58	or		~100—200	~250—300
$CsClF_4$	31.10	$MCl+2F_2=MClF_4$	90—300	—	~350—400
NH_4ClF_4	58.69	$NH_4F+ClF_3=NH_4ClF_4(?)$	25		~0—5
$NaBrF_4$	42.48	$NaF+BrF_3=NaBrF_4$	120	—	80
$KBrF_4$	38.97	$MF+BrF_3=MBrF_4$		~330	~330
$RbBrF_4$	31.48	or		—	>330
$CsBrF_4$	26.32	$MBr+2F_2=MBrF_4$	90—250	—	>330
NH_4BrF_4	43.70	$NH_4F+BrF_3=NH_4BrF_4(?)$	25	—	>0
$NaBrF_6$	52.55		140	—	—
$KBrF_6$	48.92		100	—	—
$RbBrF_6$	40.80	$MF+BrF_5=MBrF_6$	100	—	—
$CsBrF_6$	34.88		100	—	>300
NH_4BrF_6	53.80	$NH_4F+BrF_5=NH_4BrF_6(?)$	25		>6
KIF_4	31.40	$MF+IF_3 \xrightarrow{CH_3CN} MIF_4$ or	—45	—	<70
$RbIF_4$	26.35	$MI+IF_5=MIF_4+I_2$ or	20	—	70
$CsIF_4$	22.63	$MI+2F_2=MIF_4$	15—250	—	>120
KIF_6	40.71	$KF+IF_5=KIF_6$ or	100.5	~200	~200
		$KNO_3+IF_5=KIF_6+\cdots$ or	100.5		
		$KF\cdot HF+IF_5=KIF_6+\cdots$	20		
$RbIF_6$	34.92	$RbF+IF_5=RbIF_6$	100.5	—	—
$CsIF_6$	30.50	$CsF+IF_5=CsIF_6$ or	100.5	—	—
		$CsI+3F_2=CsIF_6$	15—250	—	—
NH_4IF_6	44.03	$NH_4F+IF_5=NH_4IF_6(?)$	20	—	—
$KICl_3F$	6.50	$2MF+I_2+3Cl=2MICl_3F$		—	—
$RbICl_3F$	5.61	or			
$CsICl_3F$	4.92	$ICl_3+MF \xrightarrow[pH<7]{H_2O} MICl_3F$	25	172	300
NH_4ICl_3F	7.00			194	300
$CsIBrF$	5.30	$CsF+IBr=CsIBrF$	120	—	—
ClF	34.86	$Cl_2+F_2=2ClF$	250—400	—154	—
ClF_3	61.62	$Cl_2+3F_2=2ClF_3$	250—400	—77	—
ClF_5	72.80	$ClF_3+F_2=ClF_5$	30	—93	—
BrF	19.19	$Br_2+F_2=2BrF$	10	~—33	50
BrF_3	41.60	$Br_2+3F_2=2BrF_3$	15—50	7.9	—
BrF_5	54.28	$Br_2+5F_2=2BrF_5$	200	—61.7	>460
IF	13.02	$IF_3+I_2 \xrightarrow{CCl_3F} 3IF$	—78	—	>0
IF_3	30.00	$I_2+3F_2 \xrightarrow{CCl_3F} 2IF_3$	—78	—	>—35
IF_5	42.79	$I_2+5F_2=2IF_5$	20—25	9.6	>400
IF_7	51.15	$IF_5+F_2=IF_7$	250—300	5	—
F_2	100.00	$KF\cdot 2HF$: $2HF_2^- \rightleftarrows 2e=H_2+4F^-$ $2F^- \rightleftarrows F_2+2e$	100	—218	—

TABLE 2. Fluorination of certain oxides with potassium tetrafluorobromate(III).

Compound	Fluorination temperature, °C	Time required for complete fluorination, h	Compound	Fluorination temperature, °C	Time required for complete fluorination, h	Compound	Fluorination temperature, °C	Time required for complete fluorination, h
Nd_2O_3	350	1	ZrO_2	350	1	NiO	500	2
CeO_2	350	1	MnO_2	500	1	Fe_2O_3	500	5
ThO_2	400	2	Al_2O_3	400	1	CaO	500	16

By considering halogen fluorides as ionisable solvents, it is easy to show that certain groups of compounds will react in them as acids and bases, and therefore it is possible to have compounds both with the cation XF_{n-1}^{+} and with the anion XF_{n+1}^{-}. The former are acids and the latter bases. The synthesis of such complex compounds is a direct demonstration of the mechanism of the self-ionisation of halogen fluorides and comprehensive study of the compounds extends greatly our knowledge of the chemistry of complex compounds involving a complex ion consisting entirely of halogens.

A large number of acids with the complex cation XF_{n-1}^{+} are known[60-72]. Among compounds with the complex anion, bases of Group I and Group II elements are known; compounds with alkali metals, in the first place potassium, rubidium, and caesium and, to a lesser extent sodium and ammonium, are most widely represented. So far lithium fluorohalogenates have not been isolated in a pure form, although hypotheses have been put forward concerning the possibility of their existence, at least in an unstable state; this can be fully accounted for by the low radius of the cation which sets up in its vicinity a powerful electric field coordinating the most electronegative ligands of the complex anions and thereby disrupting the latter.

Among alkaline earth metals, compounds with calcium, strontium, and barium are known. The bases with beryllium and magnesium have not been synthesised so far. This is probably also to be accounted for by steric factors. Complex compounds where Ag^{+}, NO^{+}, and NO_2^{+} serve as the cations are also known[33,72-75].

The relative ease of preparation of the complex compounds of KF, RbF, and CsF, compared with other alkali metal and alkaline earth metal fluorides, should be noted. It is interesting that similar behaviour is also characteristic of the anion ClF_3O^{-}.[76]

Among the compounds of alkali metals of small dimensions, the more stable are fluorohalogenates containing a larger halogen. This conforms to the general rule which determines the stability of polyhalogenates[77]: symmetry, the presence of a cation with a large molar volume, and the location of a large electropositive atom in the centre of the anion with all other atoms electronegative.

From this standpoint, it is clear why rubidium and caesium fluorides are more readily converted into the hexafluorobromates(V) $MBrF_6$ (M = Rb, Cs) than into the tetrafluorochlorates(III) $MClF_4$ (M = Rb, Cs) and why sodium tetrafluorochlorate(III) $NaClF_4$ does not exist while small amounts of sodium tetrafluorobromate(III) $NaBrF_4$ have been detected.

Many problems involving alkali metal fluorohalogenates have remained unsolved so far and the available information is usually restricted to purely experimental data. The first serious and successful attempt to give a systematic account of alkali metal fluorohalogenates was the review of Stepin et al.[75], but these authors, who examined alkali metal anionohalogenates in general, were of course unable to systematise sufficiently widely and completely the results of studies of fluorohalogenates in particular. Furthermore, as a result of the vigorous development of precisely this branch of inorganic chemistry, many most interesting and important data were obtained in very recent investigations and were therefore of course not included in the review of Stepin et al.[75]

The present review deals with the methods of synthesis and physicochemical properties of alkali metal fluorohalogenates—compounds which are very interesting theoretically and very important in practice in view of the possibility of their employment as highly effective solid fluorinating agents.

II. ALKALI METAL FLUOROCHLORATES

The first information about the preparation of alkali metal fluorochlorates was obtained in 1950, when Bode[39,40] established that, in the interaction of elemental fluorine with potassium, rubidium, and caesium chlorides or fluorides, powerful fluorinating agents are formed, to which the author assigned the formula MF_x (M = K, Rb, Cs; $x \simeq 3$). It was suggested[78] that compounds of this type can have the formula $M^{I}[M^{III}F_4]$. None of these data were confirmed subsequently. Evidently in this case the tetrafluorochlorates(III) of potassium, rubidium, and caesium ($MClF_4$), markedly contaminated by the initial fluorides, were obtained for the first time. Chemical analysis of the synthesised compounds did not reveal the presence of chlorine, which can be explained by the fact that tetrafluorochlorates(III) form chlorate and not chloride ions on interaction with water. This was demonstrated experimentally more than ten years later[79,80] and therefore reliable data on alkali metal fluorochlorates, the methods of their synthesis and their properties, derive from publications of the last 3–5 years.

1. Alkali Metal Difluorochlorates(I)

Chlorine monofluoride is only very slightly ionised in solution, according to the equation

$$2\,ClF \rightleftarrows Cl^{+} + ClF_2^{-},$$

which is confirmed by the very low electrical conductivity of liquid ClF.[52] However, at the present time compounds have been synthesised which contain both the cation Cl^{+} [65] and the anion ClF_2^{-}.[81,82]

In 1965 it proved possible to obtain for the first time a complex compound with the anion ClF_2^{-} by the reaction of nitrosyl fluoride with chlorine monofluoride[81]:

$$NOF + ClF = NO^{+}ClF_2^{-}.$$

Nitrosyl difluorochlorate(I) $NOClF_2$ is stable in the solid state only at low temperatures. Similar salts, stable at room temperature, were synthesised by the same worker with the cation NO^{+} replaced by potassium, rubidium, and caesium[82]. The preparation of potassium, rubidium, and caesium difluorochlorates(I) was achieved by two possible reactions:

$$NO^{+}ClF_2^{-} + MF = M^{+}ClF_2 + NOF \quad \text{or}$$
$$ClF + MF = M^{+}ClF_2^{-}.$$

In the synthesis of alkali metal difluorochlorates(I) various conditions (temperature, reaction time, pressure) were used. The starting materials were the corresponding fluorides, chlorine monofluoride, and nitrosyl fluoride. The latter behaved, strictly speaking, as a catalyst for the reaction, ensuring the synthesis of $NO^{+}ClF_2^{-}$ and its further interaction with the alkali metal fluoride; the latter process liberated NOF in a free state again and it was therefore not consumed in the reaction. In some experiments caesium fluoride was subjected to a preliminary

treatment with CF_3COCH_3, which, however, did not improve the reaction and the treatment was subsequently abandoned.

The best method for the synthesis of potassium, rubidium, and caesium difluorochlorides(I) proved to consist in the direct interaction of chlorine monofluoride with the corresponding fluorides. It is noteworthy that the higher the pressure and temperature the more complete is the conversion of the fluoride into the difluorochlorate(I), but in none of the cases described was 100% conversion achieved, with synthesis of a pure substance (Table 3). On the other hand, further increase in temperature, which, it would seem, should reduce the reaction time and should ensure that the reaction goes to completion, is restricted to 230°C (the temperature limit of the thermal stability of the substances synthesised).

Attempts to prepare lithium and sodium difluorochlorates(I) by a similar method at temperatures between 25° and 150°C and pressures of the order of 140 atm were unsuccessful. Chlorine was not detected in the reaction products and X-ray diffraction studies failed to reveal the presence of substances other than the initial fluoride.

Ammonium fluoride does not react with gaseous chlorine monofluoride[83] and the use of high temperatures and pressures was not undertaken; however, even this would probably not lead to success, since ammonium difluorochlorate(I) should exist only at low temperatures, if at all.

Potassium, rubidium, and caesium difluorochlorates(I) are solid white salts with relatively high thermal stability (the decomposition temperatures of $KClF_2$, $RbClF_2$, and $CsClF_2$ are respectively 237°, 248°, and 262°C). The decrease of the size of the cation and the increase of polarisation on going from Cs^+ to Li^+ are consistent with the stability of alkali metal fluorochlorates(I). As oxidising and fluorinating agents, these compounds are somewhat inferior to the corresponding tetrafluorochlorates(III).

Infrared spectroscopic studies on caesium difluorochlorate(I)[82] revealed the presence of an absorption band at 636 cm^{-1}, which is consistent with the data obtained earlier for $NO^+ClF_2^-$ (635 cm^{-1}) and corresponds to the asymmetric vibration to the ClF_2^- anion. It is suggested that in nitrosyl difluorochlorate(I) this anion has a linear structure. A similar structure is probably typical for ClF_2^- also in alkali metal difluorochlorates(I).

X-Ray diffraction studies on potassium, rubidium, and caesium difluorochlorates(I) showed the presence of very intense lines corresponding to the α-modification of the bifluoride impurity[84], while the difluorochlorate(I) itself gives rise only to lines of low intensity or is altogether amorphous to X-rays[82].

The infrared spectroscopic data, confirming the linear configuration of the ClF_2^- anion, can be accounted for by one of the following models: (a) the hybridisation model[85], permitted mainly by the sp^3d hybridisation of the atomic orbitals of chlorine, which leads to a trigonal bipyramid with two fluorine atoms at the apex, the chlorine atom in the centre, and three free electron pairs in the remaining corners; (b) the more probable molecular orbital model[85], incorporating mainly the $p\sigma$-atomic orbitals which are used to form semi-ionic bonds.

In conclusion it should be noted that at the present time no alkali metal difluorochlorate(I) has been obtained in a pure form. The results of chemical analysis (Table 3) have been calculated from the increase in the weight of the starting material and on the assumption that the final product is a mixture of only two substances— the alkali metal fluoride and the corresponding difluorochlorate(I). However, X-ray diffraction data fail to confirm this, showing the presence of the bifluoride; furthermore, there is a possibility of a definite amount of impurities due to reaction with the walls of the vessel. Therefore the above chemical identification cannot be regarded as sufficiently reliable. On the other hand, the thermal data, the fluorinating properties of the synthesised mixtures, and also the infrared spectroscopic data (which have been obtained unfortunately only for $CsClF_2$) definitely characterise the new compounds as the difluorochlorates(I) of potassium, rubidium, and caesium.

There is no doubt that the next problem to be solved involves the finding of ways to separate the difluorochlorate(I) from the unreacted fluoride or conditions in which the reaction is successfully taken to completion with formation of a pure product. Only then will it be possible to consider further reliable and comprehensive chemical and physicochemical studies of alkali metal difluorochlorates(I).

TABLE 3. Synthesis of the difluorochlorates(I) of potassium ($KClF_2$), rubidium ($RbClF_2$), and caesium ($CsClF_2$).

Starting materials, moles			Reaction temp., °C	Duration of reaction, h	Reaction pressure, atm	Degree of conversion of initial mixture into $MClF_2$, %	Calc., %			Found, %		
fluoride	ClF	NOF					metal	Cl	F	metal	Cl	F
KF												
0.069	0.390	0.031	150	14	154.7	27	58.5	8.5	33.0	58.2	8.5	33.7
RbF												
0.047	0.200	0.047	25	24	77.3	49	68.1	10.9	21.0	68.1	10.8	20.7
0.036	0.220	—	230	60	91.4	73	61.4	16.3	22.4	60.6	15.0	22.3
0.028	0.240	0.015	230	60	112.5	87	57.4	19.4	23.2	58.2	8.2	22.4
CsF												
0.200	0.700	—	175	48	56.3	53	74.8	9.4	15.8	73.6	9.1	16.0
0.035	0.210	0.012	175	48	77.3	80	69.0	13.7	17.2	69.5	8.7	17.4

2. Alkali Metal Tetrafluorochlorates(III)

In 1961 Asprey et al.[79] showed, having repeated the experiments of Bode[39,40], that the reaction of elemental fluorine with potassium, rubidium, and caesium chlorides does not result in the formation of polyfluorides MF_x ($x \simeq 3$) but tetrafluorochlorates(III), according to the following equation:

$$MCl + 2F_2 = MClF_4.$$

Since the reaction is strongly exothermic, a temperature exceeding the thermal stability of the synthesised tetrafluorochlorate(III) is readily attained and the decomposition is accompanied by the formation of the fluoride:

$$MClF_4 = MF + ClF_3.$$

For this reason, tetrafluorochlorates(III) are very difficult to obtain in a pure form, and the substances synthesised usually contain a certain amount of the corresponding fluoride as a impurity. On the other hand, when the temperature of the synthesis is reduced, the reaction does not go to completion and the impurity is then the initial chloride.

Potassium, rubidium, and caesium tetrafluorochlorates(III) were synthesised in the temperature range 90–250°C.[79] It is noteworthy that Bode and Klesper[43], having

repeated, simultaneously with Asprey et al.[79], their earlier experiments on the fluorination of rubidium chloride with elemental fluorine and having carried out a more comprehensive identification of the substances synthesised, virtually abandoned their earlier findings concerning the formation of polyfluorides[39,40] and arrived at a conclusion analogous to that of Asprey et al.[79] They isolated[43] a substance with the composition Rb_3ClF_6 which was shown by X-ray diffraction to contain no rubidium fluoride. This compound is the double salt $2RbF.RbClF_4$.

Kelly et al.[80] investigated the reaction of alkali metal chlorides with elemental fluorine as a function of temperature (up to 300°C) and pressure (up to 4000 atm). The reaction between potassium chloride and fluorine leads to the formation of potassium tetrafluorochlorate(III) $KClF_4$ only at elevated temperatures and pressures (Table 4). At room temperature only part of the initial potassium chloride is converted into KF even at a pressure of 4000 atm, and potassium tetrafluorochlorate(III) does not form (Table 4, experiment 1).

An increase of temperature leads to the formation of $KClF_4$, the yield being higher the higher is the temperature and pressure. At 300°C and 3400 atm the starting material is completely absent from the final product, but up to 10% of potassium fluoride remains as an impurity and pure $KClF_4$ cannot be obtained (Table 4, experiment 4). Potassium tetrafluorochlorate(III) was identified chemically and by X-ray diffraction. Total chlorine, total fluorine, and potassium were determined for the chemical identification. The calculations were based on the equations

$$\%\ KF = \left(\frac{\%\ K}{39.1} - \frac{\%\ Cl}{35.5}\right) \times 58.1$$

$$\%\ KClF_4 = \frac{1}{4}\left(\frac{\%\ F}{19.0} - \frac{\%\ KF}{58.1}\right) \times 150.6$$

$$\%\ KCl = \left(\frac{\%\ Cl}{35.5} - \frac{\%\ KClF_4}{150.6}\right) \times 74.6\ .$$

Such chemical identification is undoubtedly not free from disadvantages and of course the next problem is to obtain pure potassium tetrafluorochlorate(III). X-Ray diffraction study of the substances synthesised (Table 4, experiments 3 and 4) showed the absence of potassium chloride and the presence of potassium fluoride together with a new phase—potassium tetrafluorochlorate(III).

When elemental fluorine was allowed to react with rubidium chloride (300°C, 1500 atm), a white powder containing 56.7% Rb, 30.9% F, and 11.3% Cl formed. These data and also the results of X-ray diffraction analysis show that under the conditions indicated a mixture with the composition 62.5% $RbClF_4$ + 36.2% RbF was synthesised.

The reaction of elemental fluorine with caesium chloride (300°C, 1250 atm) yielded a powder, amorphous to X-rays, the chemical analysis of which showed the presence of 61.3% Cs, 28.3% F, and 10.0% Cl (calculated for $CsClF_4$: 54.4% Cs, 31.1% F, 14.5% Cl), i.e. evidently in this case a mixture of caesium tetrafluorochlorate(III) and caesium fluoride was obtained.

TABLE 4. Synthesis of potassium tetrafluorochlorate(III) $KClF_4$ by the reaction $KCl + 2F_2 = KClF_4$.

No. of experiment	Maximum temperature, °C	Maximum pressure, atm	Results of chemical analysis, wt. %			Compounds present, wt. %		
			K	F	Cl	KCl	KF	$KClF_4$
1	25	4000	56.8	9.8	33.8	70.0	30.0	—
2	175	3600	42.9	39.8	17.3	8.7	35.4	55.9
3	300	2800	30.2	47.9	21.9	1.9	9.0	89.1
4	300	3400	28.4	50.3	21.3	—	9.6	90.4

The attempts to prepare sodium and lithium tetrafluorochlorates(III), even in a mixture with the corresponding fluoride, by the reaction of elemental fluorine with the corresponding chlorides were unsuccessful. In all cases (even at high temperatures and pressures) only the fluorides of these metals formed. The attempt to carry out the reaction of potassium fluoride with elemental fluorine (300°C, 3000 atm) to prepare potassium polyfluoride KF_n ($n > 1$) also failed.

The method of preparation of alkali metal tetrafluorochlorates(III) based on the reaction of elemental fluorine with the corresponding alkali metal chlorides at high temperatures and pressures is experimentally very difficult and leads to the formation of substances with a large amount of impurities. A more promising procedure is based on the use of chlorine trifluoride[86]. The solvolysis of alkali metal fluorides in liquid chlorine trifluoride yields the corresponding tetrafluorochlorates(III). The reaction can be described by the equations

$$2\,ClF_3 \rightleftarrows ClF_2^+ + ClF_4^-,$$

$$MF + ClF_3 = M^+ + ClF_4^-.$$

The self-ionisation of chlorine trifluoride results in the formation of the complex anion ClF_4^- which gives rise to the base $M^+ClF_4^-$ on interaction with the alkali metal.

Chlorine trifluoride free from the F_2, Cl_2, and ClF impurities and also alkali metal fluorides of high purity, which had been subjected to preliminary heat treatment to remove traces of moisture, were used in the reaction. The syntheses were achieved in a vacuum system made from Monel and nickel. The degree of conversion of the fluoride into the tetrafluorochlorate(III) was determined from the increase in weight after complete removal of excess ClF_3. Chemical analysis involved the determination of total chlorine and total fluorine. The results of the study on the behaviour of alkali metal fluorides in chlorine trifluoride are compiled in Table 5.

The data in Table 5 are completely consistent with the results of earlier work[79,80] and show that lithium and sodium tetrafluorochlorates(III) are not formed even when chlorine trifluoride is used. The conversion of potassium, rubidium, and caesium fluorides into the corresponding tetrafluorochlorates(III) with the aid of chlorine trifluoride is more complete and takes place at lower temperatures than in the reaction between elemental fluorine and the corresponding chlorides. The degree of conversion depends on the nature of the cation and is higher the greater is the size of the alkali metal cation, which is consistent with the general rule governing the stability of polyhalides[77]. The stability series for alkali metal tetrafluorochlorates(III) should evidently be as follows: Cs > Rb > K. The size of the cations NH_4^+ and K^+ (1.48 Å for NH_4^+ and 1.33 Å for K^+)[87] suggests that the conversion of NH_4F into NH_4ClF_4 in the reaction with chlorine trifluoride should be possible. However, the substance formed is unstable and decomposes with explosion when an attempt is made to isolate it in a pure form[86]. N_2, Cl_2, and NF_2Cl in various proportions were found in the explosion products[83].

It is interesting to examine the interaction in ternary systems of the type HF–MF–ClF_3 (M is an alkali metal)[86]

TABLE 5. Synthesis of alkali metal tetrafluorochlorates(III) using chlorine trifluoride*.

Fluoride	Molar ratio ClF_3:MF	Results of chemical analysis, wt. %		Results of analysis
		Cl	F	
LiF	8	–	–	Does not react
NaF	8	–	–	Does not react
KF	8	14.7	46.7	A white crystalline substance forms, 56.5% of the initial KF being converted into $KClF_4$. Calculated for the composition $KClF_4.0.8KF$: 18.2% Cl; 46.5% F.
RbF	7	15.4	37.3	A crystalline solid substance forms, 85.2% of the initial RbF being converted into $RbClF_4$. Calculated for the composition $RbClF_4.0.2RbF$: 16.5% Cl; 36.9% F.
CsF	8	14.4	30.8	A solid crystalline substance forms, 91% of the initial CsF being converted into $CsClF_4$. Calculated for the composition $CsClF_4.0.1CsF$: 13.7% Cl; 30.0% F.
NH_4F	–	–	–	$NH_4F + ClF_3$ mixture explodes on heating above 0°C. The unstable ammonium tetrafluorochlorate(III) NH_4ClF_4 probably forms.

* The reactions were carried out at 100°C.

in order to test the possibility of synthesising alkali metal tetrafluorochlorates(III) in this way. Chlorine trifluoride was added to solutions of the alkali metal fluoride in liquid hydrogen fluoride, the molar ratio MF : HF being chosen so that the alkali metal fluoride was completely dissolved. With lithium fluoride and sodium fluoride, only the bifluorides were obtained. On the other hand, when potassium fluoride, rubidium fluoride, and caesium fluoride were used, the products were solvated bifluorides. Thus in all cases the compounds obtained were the same as those synthesised earlier in the binary systems HF–MF;[88-92] there was no addition of ClF_3, and chlorine was completely absent from the products. These results contradict the data concerning the existence of complexes of HF and ClF_3 [93,94] but are consistent with later data, according to which chlorine trifluoride behaves in hydrofluoric acid as a strong base[95], which favours the formation of stable bifluoride ions[96]:

$$2\,HF + ClF_3 \rightleftarrows ClF_2^+ + 2\,HF_2^-,$$

i.e. its behaviour is analogous to that of alkali metal fluorides in liquid hydrogen fluoride:

$$MF + HF \rightleftarrows M^+ + HF_2^-.$$

It now becomes quite clear why tetrafluorochlorates(III) were not obtained under these conditions. The concentrations of the alkali metal fluorides in liquid hydrogen fluoride solutions correspond to their solubilities[97,98]:

$$CsF > RbF > KF > NaF > LiF.$$

Potassium, rubidium, and caesium tetrafluorochlorates(III) are white crystalline substances which melt at about 100–200°C and decompose into the alkali metal fluoride and gaseous products on heating in a vacuum or in an inert medium at 350–400°C.[86] According to infrared spectroscopic data, the gaseous products are ClF_3 and ClF. The infrared spectrum of solid potassium tetrafluorochlorate(III) showed the presence of the 1970, 1830, 1225, and 970 cm^{-1} frequencies. Caesium tetrafluorochlorate(III) is diamagnetic.

X-Ray diffraction study of potassium tetrafluorochlorate(III) led to its assignment to the tetragonal system with the lattice constants $a = 6.18$ and $c = 10.94$ Å. The type of the unit cell is evidently that of potassium perchlorate, but the crystallisation of alkali metal tetrafluorochlorates(III) is not entirely similar to that of the corresponding perchlorates. Rubidium tetrafluorochlorate(III) crystallises in the cubic system with $a = 4.30$ Å and the unit cell is tentatively assumed to be of the caesium chloride type. As mentioned above, caesium tetrafluorochlorate(III) is amorphous to X-rays.

Potassium tetrafluorochlorate(III) decomposes at about 200°C, while caesium tetrafluorochlorate(III) can be heated for several hours at 300°C without decomposition. As regards thermal stability, rubidium tetrafluorochlorate(III) is intermediate between the tetrafluorochlorates(III) of potassium and caesium.

The densities of potassium and caesium tetrafluorochlorates(III), containing a certain amount of the fluorides as impurities, are as follows[86]:

$$d_4^{25} = 2.58 \text{ for } KClF_4.0.8KF,$$

$$d_4^{24} = 3.40 \text{ for } CsClF_4.0.1CsF.$$

The densities of pure potassium and caesium tetrafluorochlorates(III) can be calculated on the basis of additivity (assuming that the specimens are $MClF_4 + MF$ mechanical mixtures)—the corresponding values are 2.61 and 3.39.

The high oxidising power of alkali metal tetrafluorochlorates(III) must be regarded as their main chemical property[86]. They react vigorously with water, the reaction resulting in the evolution of oxygen and the formation of chlorate ions.

Iodates are oxidised by tetrafluorochlorates(III) to iodine. The chemical reactivity of the compounds is inversely proportional to their stability, which can be represented by the following general scheme:

$$\xrightarrow{\text{increase of stability}}$$
$$K—Rb—Cs$$
$$\xleftarrow{\text{increase of chemical reactivity}}$$

It is known that Pyrex glass does not react with chlorine trifluoride free from hydrogen fluoride, but a solution of an alkali metal fluoride in ClF_3 breaks down Pyrex glass very vigorously, which is evidently due to the increased self-ionisation of chlorine trifluoride as a result of the shift of the equilibrium

$$2\,ClF_3 \rightleftarrows ClF_2^+ + ClF_4^-.$$

Thus it may be suggested that solutions of alkali metal fluorides in chlorine trifluoride can serve as fluorinating agents more powerful than liquid chlorine trifluoride.

Alkali metal tetrafluorochlorates(III) char wood and paper on contact and react explosively with many organic substances.

As a result of their low vapour pressure, alkali metal tetrafluorochlorates(III) can be used in fluorination reactions at temperatures up to 500°C without the development of a high pressure in a closed system, i.e. these compounds find application as convenient sources of fluorine in those reactions where it is difficult to use liquid or gaseous chlorine trifluoride and other halogen fluorides.

In view of their unusual nature, high oxidising power, and high fluorine content, alkali metal tetrafluorochlorates(III) are the most interesting compounds among all the fluorohalogenates known at the present time. It is interesting to examine the behaviour of these compounds as bases and

their interaction with various acids and to investigate the mechanism of the hydrolysis, fluorination processes, etc. However, it should be noted that the chemistry of alkali metal tetrafluorochlorates(III) has been investigated very little and that all the problems enumerated above remain unresolved so far. Information about the physical properties is also very limited. Furthermore, alkali metal tetrafluorochlorates(III) free from the fluorides as impurities have not been synthesised and the nature of the impurities has not been established (i.e. whether these substances are present as mechanical mixtures or whether they are compounds of the double salt type). All these are the most interesting and promising problems awaiting solution in the further study of alkali metal tetrafluorochlorates(III).

As regards alkali metal fluorochlorates in general, it should be noted that the most promising and important task at the present time is the synthesis of hexafluorochlorates(V) with the general formula $MClF_6$, where M is the alkali metal. The information about chlorine pentafluoride is limited to three brief communications[25,99,100] and the reliable synthesis of chlorine pentafluoride was developed as late as 1966.[25] Evidently, as for other fluorochlorates[52,53], the phenomenon of self-ionisation in solution is characteristic of chlorine pentafluoride:

$$2\,ClF_5 \rightleftarrows ClF_4^+ + ClF_6^-$$

which means that there is a possibility of the formation of acids and bases containing the corresponding complex ions. Bases of this type should be the most powerful solid fluorinating agents among those known at the present time.

III. ALKALI METAL FLUOROBROMATES

The reaction leading to the formation of alkali metal fluorobromates was first achieved by Moissan[101], who observed the formation of a compound of fluorine and bromine on fluorination of potassium bromide with gaseous fluorine. Potassium tetrafluorobromate(III) $KBrF_4$ was probably obtained but the compound was not isolated in a pure state; under the experimental conditions used $KBrF_4$ decomposed into potassium fluoride and bromine trifluoride, which was in fact the new, hitherto unknown compound of fluorine and bromine.

The following compounds of bromine and fluorine are known[102-105]: bromine monofluoride BrF, bromine trifluoride BrF_3, and bromine pentafluoride BrF_5. Bromine monofluoride has not yet been isolated in a pure form: it is the least stable compound of the three enumerated above, which is why it has not been well characterised physicochemically. Its chemical properties have not been much investigated either, since it is difficult to separate it from BrF_3, BrF_5, and Br_2 which are in equilibrium with it. Evidently this is the reason why alkali metal difluorobromates(I) have not been isolated so far. Analogous derivatives of BrF_3 and BrF_5 have been successfully synthe- and their properties have been vigorously investigated in recent years.

Banks et al.[52] observed experimentally a considerable difference (by a factor of about 100) between the electrical conductivities of bromine trifluoride in the solid and liquid state; they believe that this is evidence of the ionic character of the conductivity of bromine trifluoride. In view of this and also a number of chemical properties of bromine trifluoride, self-ionisation according to the following equation has been suggested:

$$2\,CrF_3 \rightleftarrows BrF_2^+ + BrF_4^- .$$

The analogous behaviour of bromine pentafluoride is also quite evident:

$$2\,BrF_5 \rightleftarrows BrF_4^+ + BrF_6^- .$$

Thus successful synthesis of two types of alkali metal fluorobromates, containing the anions BrF_4^- and BrF_6^-, was to be expected. Representatives of both classes are in fact known: alkali metal tetrafluorobromates(III) and hexafluorobromates(V).

1. Alkali Metal Tetrafluorobromates(III)

The determination of the nature of liquid bromine trifluoride and its solutions served as a basis for the successful synthesis of alkali metal tetrafluorobromates(III).[52,53,106-109] Bromine trifluoride can behave both as a donor and acceptor of electrons. The data on the solubility of alkali metal halides in bromine trifluoride are very important for the elucidation of the conditions in which alkali metal tetrafluorobromates(III) can be synthesised. The solubility is of the ionic type. On dissolution in bromine trifluoride, alkali metal fluorides are almost completely dissociated into ions, the solubility increasing sharply with the atomic weight of the metal[110]. When an alkali metal fluoride dissolves, the anion BrF_4^- forms in accordance with the equation

$$MF + BrF_3 = M^+[BrF_4^-] .$$

Thus bromine fluoride behaves in this case as an acceptor of fluoride ions. It is interesting that similar behaviour is also characteristic of hydrogen fluoride:

$$MF + HF = M^+[HF_2^-] .$$

Sharpe and Emeléus[107] investigated the reactions of bromine trifluoride with alkali metal halides. With lithium chloride, double decomposition results in the formation of lithium fluoride, which is sparingly soluble in an excess of bromine trifluoride. When sodium fluoride is dissolved in bromine trifluoride and when the excess of the latter is removed in a vacuum, a compound with the composition $NaF.0.97BrF_3$ forms. Evidently sodium tetrafluorobromate(III) with an admixture of sodium fluoride is obtained in this case. Potassium chloride is appreciably soluble in bromine trifluoride, the dissolution involving more profound transformations than is the case with lithium fluoride; this is confirmed by the isolation of the reaction product in a pure state. When the excess solvent is removed (vacuum 130°C), a white crystalline substance remains, whose composition corresponds to the formula $KBrF_4$. Sharpe and Emeléus[107] also point out the possibility of preparing the analogous rubidium and caesium salts; however, it was not possible to isolated these compounds in a pure state.

The data for ammonium fluoride show that the compound NH_4BrF_4 is unstable and decomposes explosively. However, ammonium tetrafluorobromate(III) NH_4BrF_4 should be much more stable than ammonium tetrafluorochlorate(III) NH_4ClF_4, and it is quite evident that its isolation in a pure form is possible. So far this compound has not been isolated and investigated. There are only data showing that the interaction of ammonium fluoride with bromine trifluoride yields a white solid product with the tentative composition NH_4BrF_4.[86] Apart from the reaction between alkali metal fluorides or chlorides with liquid bromine trifluoride, alkali metal tetrafluorobromates(III) can be prepared by a "dry" method involving the reaction

$$MBr + 2\,F_2 = MBrF_4 .$$

The tetrafluorobromates(III) of potassium, rubidium, and caesium were obtained in this way[79]. This method was first used by Bode[39,40], but the latter incorrectly identified the reaction products, as in the case of the chloride.

Thus potassium, rubidium, and caesium tetrafluorobromates(III) have so far been isolated in a pure form, sodium tetrafluorobromate(III) has been obtained together with impurities, and it has been suggested that ammonium tetrafluorobromate(III) may be obtained.

Alkali metal tetrafluorobromates(III) are white crystalline involatile substances. For example, when potassium tetrafluorobromate(III) was placed in a quartz tube and evacuated at room temperature for 6 h, the weight loss was only 0.5%. At 158°C the vapour pressure of $KBrF_4$ is 20 mmHg and at 356°C it is only 90 mmHg. In the above temperature range the vapour pressure is described by the equation

$$\lg P_{mm} = 3.38 - \frac{890}{T}.$$

When potassium tetrafluorobromate(III) is heated at 200°C for 5 min, the weight loss is 30%, while sodium tetrafluorobromate(III) decomposes completely under these conditions; furthermore, rapid decomposition of $NaBrF_4$ is observed even at 80°C. This is one of the reasons for the difficulty of synthesising pure sodium tetrafluorobromate(III).

The melting point of $KBrF_4$ has been determined approximately–it is near 330°C. When the substance is heated above 330°C, the vapour pressure rises sharply, which can be explained by the decomposition of $KBrF_4$ with evolution of gaseous BrF_3.

Thermal decomposition of potassium tetrafluorobromate(III) is accompanied by the evolution of BrF_3 and the formation of potassium fluoride. Similar thermal decomposition is in general characteristic of analogous compounds, i.e. the more electronegative halogen remains in a compound with the alkali metal. This rule is also evident in the thermal decomposition of $KICl_4$ and $RbICl_3F$. The thermal decomposition of these compounds is accompained by the evolution of ICl_3 and the formation of potassium chloride and rubidium fluoride respectively[111,112].

This general tendency in the decomposition of polyhalogenates is explained by the fact that the lattice energy of the alkali metal halides decreases on going from the fluorides to iodides and therefore the formation of the halides involving the most electronegative halogen is favoured by the energy change.

There are no data on the thermal stability of rubidium and caesium tetrafluorobromates(III). The stability series should however be the same as for the tetrafluorochlorates(III), i.e. Cs > Rb > K > Na > Li. The data for $KBrF_4$ and $NaBrF_4$ fully confirm this hypothesis. The first views concerning the structure of potassium tetrafluorobromate(III) were put forward by Sharpe and Emeléus[107]. It was suggested that $KBrF_4$ has a structure analogous to that of $KICl_4$, which was found to consist of the cation K^+ and a planar anion $[ICl_4^-]$.[113] Potassium fluoride lines are absent from the powder diffraction pattern. If the $[BrF_4^-]$ anion has a configuration analogous to that of $[ICl_4^-]$, then the first is much smaller than the second, because the Br–F distance should be 1.78 Å and the I–Cl distance 2.34 Å. Subsequently a complete investigation of the crystal structure of $KBrF_4$ was made[51,114] and it was shown that the compound crystallises with a tetragonal unit cell ($a = 6.174$, $c = 11.103$ Å), the space group being $I4/mcm$. Experimental determination of the density (3.06) showed that 4 molecules are present in the unit cell, which is in good agreement with the density calculated from the X-ray diffraction data. The fluorine atoms are disposed tetrahedrally with respect to each bromine atom, with a Br–F distance of 1.81 Å. The F–F distances in the $[BrF_4^-]$ anion are 2.81 and 3.03 Å. Each potassium atom is linked to eight fluorine atoms, the K–F distances being 2.84 Å. These results were obtained from powder diffraction patterns of potassium tetrafluorobromate(III).

Sly and Marsch[115] believe that the more likely configuration is a square $[BrF_4^-]$ anion. The fluorine atoms give rise to approximately square symmetry with respect to potassium atoms. The interatomic distances in this case are as follows: Br–F 3.30, K–F 2.74, and F–F 2.70 Å. However, the authors themselves note[115] that, on the basis of the available experimental data, it is difficult to establish reliably the validity of one of the two proposed structures. The experimental results correspond with approximately the same precision to both the tetrahedral and the square configuration of the $[BrF_4^-]$ anion. The final determination of the structure of $KBrF_4$ will evidently be possible after studies on single crystals. There have been no investigations of the structures of other alkali metal tetrafluorobromates(III).

Potassium tetrafluorobromate(III) is a very reactive substance which reacts vigorously with water. The reaction products are bromine, hydrobromic and hydrofluoric acids, oxygen, and potassium fluoride. The first stage of the reaction can be represented by the equation

$$K^+BrF_4^- + 2H_2O = K^+ + HBrO_2 + 3H^+ + 4F^-\,\dagger$$

with subsequent decomposition of $HBrO_2$ into Br_2, HBr, and O_2.

$KBrF_4$ does not react with carbon tetrachloride, acetone, and dioxan and does not dissolve in them, whereas BrF_3 reacts very vigorously, usually explosively. On the other hand, even boiling BrF_3 does not react with platinum, while $KBrF_4$ does react with platinum on heating, with formation of K_2PtF_6.

$AgBrF_4$ and $Ba(BrF_4)_2$ are known to be more reactive than $KBrF_4$, due to their lower stability and the greater ease of evolution of BrF_3, which is the active principle in the reaction of these compounds. Consequently sodium tetrafluorobromate(III) should be more reactive and rubidium and caesium tetrafluorobromates(III) less reactive than potassium tetrafluorobromate(III), but no experimental data are available for these compounds.

It must be emphasised that the available experimental data refer in the first place to $KBrF_4$. The information about the tetrafluorobromates(III) of other alkali metals is restricted virtually only to the method of synthesis. All other properties can be considered only on the basis of analogies in the series Li–Na–K–Rb–Cs. Therefore so far there has been no reliable and comprehensive physicochemical study of alkali metal tetrafluorobromates(III).

† It is interesting to compare this reaction with the reaction $BrF_3 + H_2O = HBrO_2 + 3H^+ + 3F^-$.

2. Alkali Metal Hexafluorobromates(V)

The hexafluorobromates(V) of potassium ($KBrF_6$), rubidium ($RbBrF_6$), and caesium ($CsBrF_6$) were first obtained in 1964 by Whitney et al.[86] in a detailed study of the solvolysis of BrF_5. The mechanism of the interaction of alkali metal fluorides with BrF_5 involves the reactions

$$2\,BrF_5 \rightleftarrows BrF_4^+ + BrF_6^+,$$

$$MF + BrF_5 = M^+ + BrF_6^-,$$

where M is the alkali metal. The ease of reaction depends on the nature of the cation. Table 6 gives the conditions for the synthesis of alkali metal hexafluorobromates(V).

It is evident from Table 6 that the general rule common to all the alkali metal fluorohalogenates applies to hexafluorobromates(V) as well, i.e. the ease of the reaction $MF \rightarrow MBrF_6$ increases in the series Li–Na–K–Rb–Cs. The pure hexafluorobromate(V) has been obtained only for caesium, while lithium hexafluorobromate(V) does not form and sodium hexafluorobromate(V) has been obtained only as a small amount of impurity in the bulk of sodium fluoride which has not reacted.

Alkali metal hexafluorobromates(V) are white crystalline substances. They are unusually stable to heat, compared with alkali metal polyhalides without fluorine. For example, it has been shown that $CsBrF_6$ can be heated to 300°C for several hours without appreciable decomposition. The density of $CsBrF_6$ is 3.68, the density of the composition $RbBrF_6 . 0.1RbF$ is 3.59, and the value calculated for pure $RbBrF_6$ on the basis of additivity is 3.58.

Alkali metal hexafluorobromates(V) are very reactive, their hydrolysis involving the formation of bromate ions predominantly. These compounds are very powerful fluorinating agents, and since they are stable on heating to at least 300°C, their employment in high-temperature fluorination processes appears to be highly desirable.

The most important problems involving fluorobromates are those that have already been noted for fluorochlorates, i.e. they include the search for methods of synthesis of these compounds in a pure form, the determination of the nature of the mixtures synthesised, containing a definite amount of the initial alkali metal fluoride, a comprehensive physicochemical investigation of the compounds, and also the development of methods for the synthesis of alkali difluorobromates(I), which have not been obtained so far.

TABLE 6. Synthesis of alkali metal hexafluorobromates(V) using bromine pentafluoride*.

Fluoride	Molar ratio BrF_5 : MF	Results of analysis, wt. %		Results of synthesis
		Br	F	
LiF	10	–	–	Does not react.
NaF	10	–	–	No reaction observed; sodium hexafluorobromate(V) probably forms at 140°C but the degree of conversion is less than 5%.
KF	10	25.2	43.5	A white crystalline substance forms; 49.4% of the initial KF is converted into $KBrF_6$. Calculated for $KBrF_6 . KF$: 27.3% Br; 45.4% F.
RbF	10	27.3	39.8	A white crystalline substance forms; 90% of the initial RbF is converted into $RbBrF_6$. Calculated for the composition $RbBrF_6 . 0.1RbF$: 27.6% Br; 40.8% F.
CsF	10	24.4	34.8	A white crystalline substance forms; 100% conversion of CsF into $CsBrF_6$. Calculated for $CsBrF_6$: 24.4% Br; 34.8% F.
NH_4F	–	–	–	A white crystalline substance forms, but breaks down on heating above 0°C. Probably NH_4BrF_6.

* The reaction was carried out at 100°C.

IV. ALKALI METAL FLUOROIODATES

Iodine fluorides constitute the most extensive class of halogen fluorides. Iodine monofluoride IF, trifluoride IF_3, pentafluoride IF_5, and heptafluoride IF_7 are known[116–120]. Iodine heptafluoride is the only compound, not only among halogen fluorides but among interhalogen compounds in general, which contains seven atoms of one halogen in the molecule. Iodine is the only halogen which in its reaction with fluorine exhibits the highest valence characteristic of the Group. The capacity to form higher molecular species can be explained by the position of the elements in the Periodic System: the wide separation of the halogens facilitates the preparation of higher interhalogen compounds. The reason is the enhanced difference between the properties of the elements which facilitates their mutual saturation on interaction. The geometrical factor is also important: the large atomic radius of iodine and the small atomic radius of fluorine favour the maximum saturation of iodine by fluorine.

Despite the very wide variety of iodine fluorides, alkali metal fluoroiodates have been investigated least completely, which in the first place is evidently due to the low fluorinating activity of iodine fluorides, compared with chlorine and bromine fluorides.

1. Alkali Metal Tetrafluoroiodates(III)

Alkali metal tetrafluoroiodates(III) were first synthesised in 1960 by Hargreaves and Peacock[121]. The authors used IF_5 for the synthesis instead of iodine trifluoride (evidently because of the low fluorinating capacity of the latter and the low solubility of alkali metal fluoride in it). The use of IF_5 became possible after it had been established that a solution of an alkali metal fluoride in iodine pentafluoride behaves as a reducing agent, capable of reducing, for example, MoF_6 to MoF_6^- and ReF_6 to ReF_6^-.[122,123] Since the I^- ion does not exist in the solution, it is evident that the reducing agent in this case is a new complex, i.e. the tetrafluoroiodate(III) ion $[IF_4^-]$.

In the synthesis of alkali metal tetrafluoroiodates(III) with iodine pentafluoride a large excess of the latter was condensed on to the iodide of the corresponding alkali metal. The interaction was accompained by the evolution of free iodine:

$$5MI + 4F_5 = 5MIF_4 + 2I_2 .$$

After the complete dissolution in the cold of the initial solid, the excess solvent was removed in a vacuum and the reaction product was heated in the vacuum to 50°C to remove the residual iodine. Tetrafluoroiodates(III) with the general formula MIF_4 were obtained in this way for potassium, rubidium, and caesium, and also a soluble compound of caesium with the composition $CsIF_4 . IF_5$ (CsI_2F_9) (Table 7).

Alkali metal tetrafluoroiodates(III) were also synthesised using iodine trifluoride[124]. The alkali metal fluoride dissolved in acetonitrile was treated with iodine trifluoride for a long period at −45°C. Chemical analysis of

TABLE 7. Synthesis of alkali metal tetrafluoroiodates(III) using iodine pentafluoride.

Starting materials	Temperature of synthesis, °C	Products	Results of chemical analysis			
			calc., %		found, %	
			F	I	F	I
NaI+IF_5	20	—	—	—	—	—
KI+IF_5	20	KIF_4	31.4	52.5	33.0	45.3
RbI+IF_5	20	$RbIF_4$	26.3	44.1	26.2	43.3
CsI+IF_5	20	CsI_2F_9	30.7	45.5	30.7	46.6
CsI_2F_9	100 (vacuum)	$CsIF_4$	22.6	37.8	24.8	37.9

* Erroneous values were quoted by Hargreaves and Peacock [121] for the calculated iodine content of the tetrafluoroiodates(III): 48.4% for KIF_4, 44.6% for $RbIF_4$, 46.3% for CsI_2F_9, and 38.7% for $CsIF_4$. The corrected results are given in this table. It should be noted that they do not alter fundamentally the experimental data obtained for the tetrafluoroiodates(III) of rubidium and caesium and confirm the successful synthesis of these compounds. Hargreaves and Peacock [121] evidently also obtained potassium tetrafluoroiodate(III) but with considerable admixtures of the hexafluoroiodate(V), which is confirmed by the results of chemical analysis—the low iodine content and the high fluorine content of the substance synthesised.

the resulting colourless finely crystalline powders confirmed the formation of compounds with the composition MIF_4 (Table 8).

It has been stated, without the description of the conditions of synthesis, that the tetrafluoroiodates(III) of potassium, rubidium, and caesium can also be obtained using elemental fluorine to fluorinate the corresponding iodates [79]. It is surprising that the authors [79] obtained under these conditions tetrafluoroiodates(III) and not hexafluoroiodates(V). The latter is the more likely, but, in view of the brevity of the information given and the lack of identification of the products, it is impossible to assess the conclusions with sufficient reliability [79].

The tetrafluoroiodates(III) of lithium, sodium, and ammonium have not been obtained. The known alkali metal tetrafluoroiodates(III) are readily decomposed by atmospheric moisture and water. Their stability depends, as with other fluorohalogenates, on the size of the cation, which is confirmed by data derived from thermal studies. The tetrafluoroiodates(III) of potassium, rubidium, and caesium readily decompose on heating. Potassium tetrafluoroiodate(III) decomposes slowly even at room temperature with evolution of iodine, but caesium tetrafluoroiodate(III) is much more stable to heat and does not undergo appreciable changes on heating in a vacuum to 120°C. Vigorous decomposition is observed on heating below 70°C for KIF_4, below 70°C for $RbIF_4$, below 60°C for CsI_2F_9, and above 120°C for $CsIF_4$. [124] The powder diffraction patterns of potassium, rubidium, and caesium tetrafluoroiodates(III) did not permit the determination of the structures of these compounds, but they confirmed unambiguously that they do not have the same structures as the corresponding tetrafluorobromates(III). [51,114,115]

TABLE 8. Synthesis of alkali metal tetrafluoroiodates(III) using iodine trifluoride.

Compound	Results of chemical analysis					
	calc., %			found, %		
	metal	F	I	metal	F	I
KIF_4	16.1	31.4	52.5	17.3	30.5	52.0
$RbIF_4$	29.6	26.3	44.1	28.8	26.9	44.3
$CsIF_4$	39.6	22.6	37.8	39.8	23.6	36.5

2. Alkali Metal Hexafluoroiodates(V)

Iodine pentafluoride is appreciably inferior as a fluorinating agent to chlorine and bromine trifluorides. However, it too is capable of self-ionisation in solution [52,53,66,125]:

$$2\,IF_5 \rightleftarrows IF_4^+ + IF_6^-,$$

which means that the formation of acids and bases containing the corresponding complex ions is probable.

Sharpe and Emeléus [107] first showed in 1948 that potassium fluoride dissolves in IF_5 (about 1% KF) with the probable formation of potassium hexafluoroiodate(V) KIF_6. Subsequently the same workers [126] successfully achieved the synthesis of KIF_6 and examined the behaviour of other fluorides on dissolution in iodine pentafluoride.

Boiling IF_5 dissolves up to 1% of KF and on cooling white crystals are deposited from the solution. The attempt to remove the solvent at a reduced pressure (< 1 mmHg) did not result in the isolation of potassium hexafluoroiodate(V) in a pure form; phases of variable composition were produced (KF. $0.61IF_5$, KF. $0.91IF_5$). A product of constant composition was obtained by removing the excess IF_5 at 15–20°C and a pressure of 2–5 mmHg. Under these conditions the substance synthesised does not decompose and has the composition KIF_6. Potassium hexafluoroiodate(V) can also be obtained on prolonged boiling of potassium nitrate in iodine pentafluoride with subsequent removal of the excess of the latter in a vacuum at 20°C. [127]

When equimolar amounts of IF_5 and KF.HF are dissolved in anhydrous hydrogen fluoride, a deposit forms, whose composition has not been established accurately, but chemical analysis suggests that in this case too the product is KIF_6, contaminated with the initial KF.HF. [66] It is interesting to note 40% hydrofluoric acid converts KIO_3 into KIO_2F_2. [128] This compound may be regarded as the product of the partial replacement of fluorine by oxygen in potassium hexafluoroiodate(V). Caesium hexafluoroiodate(I) was obtained, like KIF_6, by crystallisation from solution in iodine tetrafluoride [126,129]. Furthermore, it has been stated that this compound can be obtained by fluorinating caesium iodide with elemental fluorine [79].

As already mentioned, when an alkali metal iodide reacts with cold IF_5, the tetrafluoroiodate(III) forms. On the other hand, the corresponding hexafluoroiodate(V) is produced in hot iodine tetrafluoride [121]. The alkali metal iodide is treated with an excess of IF_5, the solution is boiled for 5 min and then rapidly cooled, and the excess of the solvent is pumped off in a vacuum. The hexafluoroiodates(V) of potassium, rubidium, and caesium have been obtained in this way.

When NH_4F is dissolved in IF_5, a white solid is formed, which probably has the composition NH_4IF_6. In view of its extreme instability, the compound was not isolated in a pure form [85]. From the point of view of finding new ways of synthesising alkali metal fluorohalogenates, it is interesting to examine the interaction of alkali metal fluorides in

TABLE 9. Synthesis of alkali metal hexafluoroiodates(V) using copper pentafluoride.

Compound	Composition			
	calc., %		found, %	
	I	F	I	F
KIF_6	45.3	40.7	45.7	40.2
$RbIF_6$	38.3	34.9	38.3	35.5
$CsIF_6$	33.0	30.5	33.9	30.5

mixtures of halogen fluorides. It is known [130] that ClF_3 dissolves in IF_5 and BrF_5 and is not evolved on heating the mixture appreciably above its boiling point (60–70°C). This is undoubtedly due to interaction in solution. The effect of such complex self-ionisation in solution and the nature of the interaction between the alkali metal fluoride and the mixture of halogen fluorides can be explained on the basis of data for the relative acidities of the pair of halogen fluorides under consideration. In the stronger acids fluoride ions are coordinated to form complex anions of the type XF_n^-. It follows from the data in Table 10 that BrF_5 and IF_5 are stronger acids than ClF_3; the following reactions are involved:

$$\text{(a)}\ ClF_3 + BrF_5 \rightleftarrows ClF_2^+ + BrF_6^-,$$

$$MF + ClF_2^+ + BrF_6^- \rightleftarrows MBrF_6 + ClF_3,$$

$$\text{(b)}\ ClF_3 + IF_5 \rightleftarrows ClF_2^+ + IF_6^-,$$

$$MF + ClF_2^+ + IF_6^- \rightleftarrows MIF_6 + ClF_3.$$

The interaction of potassium fluoride with the ClF_3–BrF_5 mixture is an exception. In this case the tetrafluorochlorate(III) forms instead of the expected potassium hexafluorobromate(V). No explanation has so far been found for this phenomenon. When alkali metal fluorides are dissolved in ClF_3–BrF_3 mixtures, the reaction products should be the hexafluorobromate(III), and this is confirmed by the study of fluorine isotope exchange between ClF_3 and BrF_3 [93] which has shown that in this case chlorine trifluoride is a base and bromine trifluoride an acid:

$$ClF_3 + BrF_3 \rightleftarrows ClF_2^- + BrF_4^-.$$

Thus one of the methods of synthesising alkali metal fluorohalogenates is based on the use of mixtures of halogen fluorides as solvents. This is particularly important in the synthesis of fluoroiodates, in view of the lower fluorinating activity of iodine fluorides compared with chlorine and bromine fluorides.

TABLE 10. Interaction of alkali metal fluorides with ClF_3–BrF_5 and ClF_3–IF_5 mixtures.

Fluoride	Solvent	Temperature of synthesis, °C	Reaction products
KF	ClF_3+BrF_5	25	$KClF_4 \cdot KF$
KF	ClF_3+BrF_5	100	$KClF_4 \cdot 0{,}7\ KF$
RbF	ClF_3+BrF_5	25	$RbBrF_6 \cdot 0{,}5\ RbF$
CsF	ClF_3+BrF_5	25	$CsBrF_6 \cdot 0{,}1\ CsF$
KF	ClF_3+IF_5	100	KIF_6

Potassium hexafluoroiodate(V) KIF_6 is the first fluorohalogenate containing seven halogen atoms in the complex anion whose existence has been reliably established. There are no structural data for potassium hexafluoroiodate(V), but its properties are known and, by analogy with other similar compounds, one can reliably suggest the formula $K^+IF_6^-$. This is also quite evident for the hexafluoroiodates(V) of rubidium and caesium.

The iodine atoms in the complex anion $[IF_6^-]$ should have a valence shell of 14 electrons but only six coordination sites. This distinguishes the $[IF_6^-]$ anion from IF_7. Since $[IF_6^-]$ resembles $[SeF_6]^{2-}$ and $[TeF_6]^{2-}$, [131,132] it is possible that it has an octahedral structure. The configuration of iodine atoms in $[IF_6^-]$ is $5s^25p^25d^46s^2$ and therefore it can be suggested that $[IF_6^-]$ does not resemble other polyhalide anions, where the bond length is the sum of the corresponding radii [133], and that in this case the distance between the halogen atoms should be anomalously large [126].

Structural studies on KIO_2F_2 [128] have shown that the $IO_2F_2^-$ ion is an octahedron or a trigonal bipyramid. The iodine and oxygen atoms lie in one plane, the O–I–O angle is 100°±10°, and two fluorine atoms, forming an angle of 180°, are located in a direction perpendicular to the plane containing the iodine and oxygen atoms. The interatomic distances are 1.93±0.05 Å for I–O and 2.00±0.05 Å for I–F.

Potassium hexafluoroiodate(V) is moderately soluble in cold IF_5 and appreciably soluble in hot IF_5. It is decomposed by water with evolution of heat according to the equation

$$IF_6^- + 3H_2O = 6F^- + IO_3^- + 6H^+.$$

Thermal decomposition is accompanied by the evolution of IF_5 and the formation of KF. The melting point of KIF_6 is about 200°C. The fusion of KIF_6 is accompained by decomposition, since vigorous evolution of iodine pentafluoride is observed. Carbon tetrachloride does not affect KIF_6, while dioxan decomposes it only slightly [126]. All these findings are evidence of the relative stability of potassium hexafluoroiodate(V).

There are no data on the chemical behaviour of rubidium and caesium hexafluoroiodates(V). One can, however, speak of the similarity of their chemical and thermal properties and their greater stability compared with potassium hexafluoroiodate(V).

The question of the existence of alkali metal octafluoroiodates(VII) so far remains open. It is known [134] that, on interaction with iodine heptafluoride and subsequent evaporation of the latter at room temperature, rubidium chloride is only partially converted into rubidium fluoride. Under these conditions sodium, potassium, and rubidium fluorides do not dissolve in IF_7. Schumb and Lynch [134] concluded that compounds of the type MIF_8 cannot form under these conditions. However, this conclusion does not disprove the possibility of achieving the synthesis of similar compounds under other conditions; the compounds are the first representatives of bases containing nine halogen atoms in the complex anion. The synthesis of alkali metal octafluoroiodates(VIII), the search for new methods of synthesising and purifying tetrafluoroiodates(III) and hexafluoroiodates(V), the study of the physical and chemical properties of fluoroiodates, and the determination of their fluorinating capacity are the most important problems which must be solved first in further studies on alkali metal fluoroiodates.

V. ALKALI METAL FLUOROPOLYHALOGENATES

The first note concerning alkali metal fluorohalogenates containing two halogens in addition to fluorine dates back to 1931, when Cremer and Duncan[77] published an extensive paper on alkali metal polyhalogenates. It is interesting that a stability series for polyhalogenates is quoted in this paper, but the series was established only qualitatively. For the same anion the stabilities can be arranged in the following sequence: $Na < K < NH_4 < Rb < Cs$. Cremer and Duncan[77] do not indicate the position of lithium in this series, but there is no doubt that its compounds, if they exist at all, are the least stable. Only one compound containing fluorine is quoted in the paper, namely caesium fluorobromoiodate CsIBrF, which was obtained, by the adsorption of IBr on CsF, in the form of a yellow crystalline compound. The authors do not quote the results of chemical analysis and do not prove that it is indeed a chemically individual compound which, as far as one can judge from the very brief description, was evidently not isolated in a pure form. Later communications describe the syntheses of alkali metal fluorotrichloroiodates $MICl_3F$,[112,135] which have been obtained with potassium, ammonium, rubidium, and caesium in the form of orange-yellow needle-shaped crystals. The authors state that the caesium salt is the most stable and the potassium salt the least stable. In these papers the results of chemical analyses of polyhalogenates containing fluorine are quoted for the first time but fluorine was not determined directly (it was found by difference); the methods chosen by the authors for the determination of the remaining components are not the most reliable and therefore there are not sufficient grounds to believe that these compounds exist at room temperature in a free form. It should be noted that the information about alkali metal fluoropolyhalogenates is limited to the above communications, which are more than thirty years old and the experimental data of which give rise to considerable doubt. Thus at the present time there is no reliable information about this extremely interesting class of inorganic fluorides, although the existence of similar compounds of other halogens has been reliably established and they have been investigated in detail[49,136-140].

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Fluorine compounds have a number of specific properties which make them very interesting objects of study in different branches of chemistry, such as the chemistry of volatile compounds, non-aqueous solvents, complex compounds, etc., in the theory of the chemical bond, and in the study of the structure of matter. Furthermore, fluorine compounds have found considerable application in industry. The range of their application is extremely wide, in the first place because the most active and the most inert substances are to be found among one or other class of fluorine compound. However, these substances are not usually encountered in nature: they are synthesised artificially, and therefore the preparation of fluorinating agents whereby the initial compounds can be converted into fluorides always constitutes a very important problem. Evidently it is essential to have an extensive set of fluorinating agents permitting the synthesis of fluorine compounds in a predetermined manner. Powerful oxidising agents, whereby exhaustive fluorination can be readily carried out, occupy an important place here. Such substances are, in the first place, elemental fluorine, halogen fluorides, and the alkali metal fluorohalogenates examined in the present review.

There is no doubt about the advantages of alkali metal fluorohalogenates in fluorination processes. However, these compounds have not found wide practical application at the present time, which the present author believes is primarily due to the fact that they have not been adequately investigated and that reliable methods of synthesis are altogether lacking for some alkali metal fluorohalogenates, while for others they have been developed only recently. Furthermore, many methods proposed yield the required compounds only with an admixture of the initial fluoride, which is larger the lighter is the alkali metal in the fluorohalogenate synthesised.

The most promising method for the synthesis of alkali metal fluorohalogenates is the one based on the reaction of the corresponding halogen fluorides with alkali metal fluorides. It is in fact this method which yields the purest products. It is based on a reaction in a non-aqueous medium.

At an early stage of the development of inorganic chemistry water was used almost exclusively as the reaction medium, while in modern synthetic inorganic chemistry non-aqueous media are used to an increasing extent[141-144]. Reactions in non-aqueous media can be divided into two types: (a) reactions involving the self-ionisation of the solvent (i.e. solvolysis reactions) or with direct participation of the solvent and (b) reactions which are independent of the solvent. Reactions of the first type are used in the synthesis of alkali metal fluorohalogenates—the solvent itself takes part in the reaction. In this case the correct choice of the solvent and the reaction conditions is of primary importance. The task in further studies on alkali metal fluorohalogenates on these lines consists in a comprehensive investigation of binary systems of the type alkali metal fluoride–halogen fluoride which will lead to the discovery of the most rational methods of synthesising alkali metal fluorohalogenates and will permit the investigation of their most important property—their fluorinating capacity.

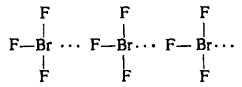
While in the initial period water was used as the sole medium in synthetic inorganic chemistry and then non-aqueous solvents, nowadays there is a tendency to use mixed non-aqueous solvents[145,146]. The most interesting results under these conditions are in fact to be expected for alkali metal fluorohalogenates; the most complete information about the conditions of the synthesis and the properties of the compounds obtained can be derived from studies of the corresponding multicomponent non-aqueous systems by methods of physicochemical analysis; this is one of the most important tasks in the further development of methods for the synthesis of alkali metal fluorohalogenates.

In the reactions considered, where aprotic solvents such as halogen fluorides are used, one may apply Gutmann and Lundqvist's definition of acids and bases[147]. Alkali metal fluorides are donors of fluoride ions and behave as bases in halogen fluorides:

$$\overset{F^-}{\overbrace{KF + ClF_3}} \rightleftarrows K^+ + ClF_4^- .$$

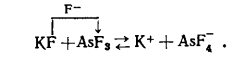
The possibility of fluoride ion transfers is determined by the structure of the compounds: for example, the BrF_3 molecule has a T-shaped configuration[148-151] while the BrF_4^- ion has a planar square structure[115,152]. The formation of fluoride bridges in pure solvents with corresponding fluoride ion transfers takes place without appre-

ciable structural changes; probably association takes place via fluoride bridges [153]:



Further structural studies should show whether the BrF_4^- ions or fluoride bridges exist in this case.

It has been shown by ^{19}F nuclear magnetic resonance that continuous fluorine exchange takes place in the KF–AsF_3 system [154]:



The ^{19}F nuclear magnetic resonance of SbF_5 solutions in AsF_3 also reveals the exchange of fluoride ions bound in fluoride bridges [154]. Consequently the presence of fluoride ions and fluoride ion coordination are characteristic of covalent solvents, which include halogen fluorides. The processes occurring in the synthesis of alkali metal fluorohalogenates using halogen fluorides should in fact be examined from these standpoints.

Thus comprehensive investigation of the reactions between halogen fluorides and alkali metal fluorides will greatly extend our knowledge about reactions in non-aqueous media, will lead to the development of reliable methods for the synthesis of alkali metal fluorohalogenates, will enable the investigation of their behaviour as oxidising agents, and will place at the disposal of theoretical and applied science new highly effective fluorinating agents.

In view of their practical value and the advances in the chemistry of alkali metal fluorohalogenates, a considerable future can be forecast for this class of inorganic fluorides.

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THE REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES

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1. INTRODUCTION

The fixation of nitrogen continues to be the subject of extensive studies in organic chemistry, biochemistry, photochemistry, electrochemistry, and radiation chemistry. This problem is vitally important, and at the same time difficult to solve. Molecular nitrogen is characterised by an unusual chemical inertness, which makes it impossible for nitrogen to react chemically with the great majority of chemical substances under ordinary conditions. The dissociation energy of nitrogen is 225.96 kcal mole^{-1} (at 298°K), the greater part of this energy (~ 125 kcal mole^{-1}) being required for the rupture of the first bond. These values are so large that they generally cannot be compensated by the liberation of energy on formation of new bonds. For example, the energies of the bonds formed by the nitrogen atom with a number of other elements have the following values (kcal mole^{-1})[1]:

N—H	N—C	N—Si	N—O	N—S	N—P	N—Sb	N—F	N—Cl	N—Br
84	195	105	152.3	116	164.9	111	61	62	70

It is clear that most fundamental reactions involving the rupture of the bonds (or even one bond) in the nitrogen molecule cannot take place spontaneously, without preliminary excitation of the molecular nitrogen. This last requirement is not simple either, however, since all the first excitation levels of molecular nitrogen are relatively high. For example, the excitation of molecular nitrogen to the first vibrational level requires an energy quantum of 0.43 eV. Thus this process will take place to a significant extent only at temperatures of the order of several thousand degrees. The energy required for the electronic excitation of N_2 amounts to not less than 6.167 eV, and that required for photochemical excitation is 8.546 eV.[2] The ionisation potential of N_2 is 15.6 eV.[1] Thus electronic excitation of nitrogen is difficult and requires extremely severe conditions. The central problem in the fixation of nitrogen is therefore the conversion of molecular nitrogen into a chemically active state. There are in principle two possibilities: (1) transfer to the nitrogen molecule of sufficient energy to bring about its electronic or vibrational excitation, dissociation, or even ionisation; (2) mild activation of molecular nitrogen; the mechanism of this process has not been elucidated, but it takes place in the fixation of nitrogen in biological systems. The second possibility has led to search for chemical systems providing models of these biological systems, and encouraging results have already been obtained[3-7]. Possible routes to chemical activation of N_2 in these systems have been examined[3,5]. Significant excitation of molecular nitrogen is achieved in the photochemical and radiation-chemical fixation of nitrogen, and also in discharge reactions. Here we are dealing with energy-rich nitrogen species such as atoms, electronically excited molecules, ions, etc. Routes to the fixation of nitrogen by organic molecules by the irradiation of these systems with hard radiation have recently been indicated[8]. In order to understand the mechanism of these complex reactions, it is important to know how the various active nitrogen species react with organic molecules. A considerable amount of factual material on these problems (particularly concerning nitrogen atoms) has accumulated, and we have tried to summarise this material in the present paper. Generally speaking, the reactions of energy-rich nitrogen species with organic molecules lead to the formation of a wide range of products. Since the present paper is concerned with the problem of nitrogen fixation, however, we shall consider here only the nitrogen-containing products of these reactions.

2. REACTIONS OF NITROGEN ATOMS

The reactions of nitrogen atoms with organic molecules will be examined chiefly on the basis of data obtained in the study of active nitrogen, that is nitrogen withdrawn from an electric discharge. The composition of active nitrogen has been the subject of detailed study since its discovery[9]. Up to the present, the following species have been identified, in addition to non-excited nitrogen molecules: $N(^4S)$, $N(^2P)$, $N(^2D)$, vibrationally excited $N_2(X^1\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$, and $N_2(a^1\Pi g)$.

The presence of nitrogen atoms in active nitrogen has been proved by a number of direct physical methods. The ultraviolet range of the absorption spectrum of active nitrogen shows the transitions $NI(^4S \rightarrow 2p^4P)$, $(^4S \rightarrow 3s^4P)$, $(2p^32D \rightarrow 3s^2P)$, and $(2p^32P \rightarrow 3s^2P)$[10].

The forbidden $NI(^2P)$ line ($\lambda = 3466$ Å) can be observed in the emission spectrum of active nitrogen at pressures

close to atmospheric [11-13]. The presence of $N(^4S)$ atoms has also been confirmed by the ESR method [14,15]. The presence of excited $N(^2P)$ and $N(^2D)$ nitrogen atoms could not be detected by this method, however (the sensitivity of the method required concentrations of paramagnetic species in active nitrogen of about 1%) [14]. Much information on the composition of active nitrogen has been obtained using mass spectrometers. The presence of both non-excited [16-23] and excited (metastable) $N(^2P)$ and $N(^2D)$ atoms in active nitrogen has been proved by this method [20,21]. The presence of nitrogen atoms in active nitrogen is very effectively demonstrated by adding nitric oxide. With increase in the rate of supply of NO to a stream of active nitrogen, the colour of the latter changes from yellow-orange through blue to greenish white, with a sharp change in colour at the moment when the N atoms are used up completely. The following reactions take place:

$$NO + N \rightarrow N_2 + O\,, \quad (1)$$

$$N + O + M \rightarrow NO\,(B^3\Pi, A^2\Sigma) + M\,, \quad (2)$$

$$NO\,(B^3\Pi, A^2\Sigma) \rightarrow NO\,(X^2\Pi) + h\nu \text{ (pale-blue luminescence)}, \quad (3)$$

$$NO + O \rightarrow NO_2 + h\nu \text{ (greenish-white luminescence)}. \quad (4)$$

Because of the high rate of reaction (1) ($k \simeq 10^{-11}$ cm^3 molecule^{-1} s^{-1}) almost all the N atoms are used up in this reaction even in the presence of a considerable excess of NO. Kistiakowsky and Volpi [24] suggested this reaction for the determination of the concentration of nitrogen atoms in active nitrogen. The correctness of this procedure was subsequently confirmed by a number of workers: (a) by comparison of the concentration of nitrogen atoms determined by titration with nitric oxide with the value found from the decrease in pressure in an abruptly isolated volume containing active nitrogen [25]; (b) by determination of the equivalence point using the ESR method [15]; and (c) by comparison of the heat liberated in the deactivation of the active species on a cobalt surface with the expected value, calculated on the assumption that only the N atoms whose concentration was determined by titration with nitric oxide are removed on the surface [26].

The concentration of nitrogen atoms in active nitrogen depends on the type of discharge used for the excitation. The active nitrogen withdrawn from a microwave or ultra-high frequency discharge contains $\sim 1\%$ of nitrogen atoms, whereas that withdrawn from a condensed discharge contains up to 100% of nitrogen atoms [27]. Most of the atoms are in the ground (^4S) state. Estimation of the relative concentrations of nitrogen atoms in various excitation states, carried out by spectroscopic [10] and mass-spectrometric [20,21] methods, gave results showing satisfactory agreement and indicated that the concentration of $N(^4S)$ is greater than the concentration of $N(^2P)$ and $N(^2D)$ by 2-3 orders of magnitude. These data relate to the composition of active nitrogen about 1×10^{-3} s after it has left the discharge tube. At later stages of the afterglow, metastable nitrogen atoms cannot be detected at all [20,21]. This is apparently due to the rapid deactivation of the excited atoms on the walls.

Vibrationally excited nitrogen molecules in the ground electronic state ($X^1\Sigma_g^+$) have been observed in active nitrogen by spectroscopic methods. Dressler [28] recorded in the absorption spectrum nine bands from the Lyman-Birge-Hopfield (L-B-H) system ranging from (0,0) to (0,8). In a number of studies of the absorption spectra of the so-called pink afterglow of active nitrogen which lasts about 1×10^{-3} s, it was shown that this nitrogen contains a large quantity of $N_2(X^1\Sigma_g^+)$, excited to high vibrational levels (up to $v = 29$) [29,32]. On the basis of an analysis of ionisation curves for N_2^+, obtained by the mass-spectrometric method, Foner and Hudson [20,21,33] concluded that in the early stages active nitrogen contains $N_2(X^1\Sigma_g^+)$ molecules, whose vibrational energy reaches 7.5 eV. Kaufman and Kelso [34] detected appreciable liberation of heat when N_2O and CO_2 were added to active nitrogen; this can be interpreted as transfer of the vibrational energy of the nitrogen molecules to translational degrees of freedom, sensitised by these additives. According to their estimate, the heat liberated amounted to ~ 2 kcal mole^{-1}, which corresponded to a vibrational energy distribution with 30% of the $N_2(X^1\Sigma_g^+)$ molecules in the vibrational level with $v = 1$. Thermochemical studies of the deactivation of active nitrogen on the surface of a cobalt catalyst confirmed the existence, in active nitrogen, of a large quantity of nitrogen molecules excited to the first vibrational level [26]. It is now assumed that the active nitrogen with which chemical reactions are usually carried out (~ 0.1 s after removal from the discharge tube) does not contain the highly excited vibrational states of $N_2(X^1\Sigma_g^+)$ molecules [35]. As with metastable nitrogen atoms, this is apparently due to the fact that N_2 molecules excited to high vibrational levels are formed only in the discharge, and before they are observed in the chemical reaction vessel they are able to redistribute their energy in collisions with non-excited nitrogen molecules. For example, 1×10^{-4} s after leaving the discharge, active nitrogen contains $N_2(X^1\Sigma_g^+)$ molecules with vibrational energy up to 7.5 eV; [33] the corresponding figures after 1×10^{-3} s and 1×10^{-2} s are 7.16 eV [29-32] and 2.36 eV [28] respectively, and after 5×10^{-2} s active nitrogen contains only N_2 in the first vibrational level ($E_{v=1} = 0.43$ eV) [26]. Estimates of the concentrations of vibrationally-excited nitrogen molecules, carried out in the early stages of the afterglow, give values which showed good agreement: 10% according to the absorption spectra [28,29] and 8% from mass-spectrometric data [33]. Study of the deactivation of vibrationally-excited nitrogen molecules in the later stages of the afterglow with the aid of N_2O has given estimated values for the concentration of $N_2(X^1\Sigma_g^+, v = 1)$ of 30% [34] and more [26].

The intense emission by bands of the first positive system of nitrogen ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) suggests that active nitrogen contains considerable concentrations of metastable $N_2(A^3\Sigma_u^+)$ molecules, since the radiative lifetime of this state, according to recent estimates, is of the order of 10 s, and its deactivation by collision with N_2 is hindered [13,36]. Nevertheless, optical transitions from this state in active nitrogen (pressure about 1 mmHg) have not been observed, either in the absorption spectra under ordinary conditions [37] or in the emission spectra [Vegard-Kaplan bands (V-K bands)] [35,38-40]. Corresponding transitions were observed in the discharge [41,42], and its was established that, in order to observe the V-K bands, it is necessary to have very pure nitrogen; traces of Hg and O_2 are particularly harmful [32]. It may be assumed that the $N_2(A^3\Sigma_u^+)$ molecules in active nitrogen are rapidly deactivated in collisions with the walls or impurities. Working with pure nitrogen, Noxon [11,13] observed fairly intense luminescence of V-K bands in active nitrogen at high pressure (up to 1 atm), when deactivation on the walls was hindered. After thorough purification of nitrogen, Zipf [36] was also able to observe V-K bands in the afterglow of nitrogen in the pressure range 0.1-10 mmHg. Young [40] concluded that nitrogen atoms can play the same role as an impurity in the deactivation of $N_2(A^3\Sigma_u^+)$ molecules. On collision, exchange by atoms takes place according to the reaction:

$$N + N_2(A^3\Sigma_u^+, v=0) \rightarrow N_2(X^1\Sigma, v=25) + N\,. \quad (5)$$

According to his estimates, this reaction takes place very rapidly ($k = 2 \times 10^{-10}$ cm^3 s^{-1}). This might have explained the decrease in the intensity of the V–K bands with increase in the concentration of nitrogen atoms [13,36]. If Young is correct, however, it is difficult to understand why $N_2(X^1\Sigma_g^+)$ molecules, excited to high vibrational levels, cannot be detected in the afterglow after 5×10^{-2} s. The greater intensity of the V–K bands compared with the first positive system of nitrogen, observed by Noxon and Zipf, suggests that there exist other sources of $N_2(A^3\Sigma_u^+)$ molecules in addition to recombination of atoms. One such source is undoubtedly the discharge. This is indicated by the results of mass-spectrometric studies [20,33], in which it was established that $N_2(A^3\Sigma_u^+)$ molecules are present in active nitrogen in significant concentrations only 100 μs after leaving the discharge (100 μs was the lower limit in these experiments) and are observed throughout the entire time interval studied (up to 2×10^{-3} s). It is possible that $N_2(A^3\Sigma_u^+)$ molecules were detected in active nitrogen by the ESR method [43]: the authors cited observed the ESR spectrum of paramagnetic species but the spectrum could not be assigned to nitrogen atoms or free electrons. The rate of deactivation of these species was described by a first-order kinetic equation with a half-life of 0.07 s at a pressure of 4.4 mmHg.

The presence of $N_2(B^3\Pi_g)$ in active nitrogen is evident, since the long-lived yellow afterglow, characteristic of active nitrogen, consists of first positive bands of nitrogen. The bands with $v' > 12$ are usually not observed, but it is possible to observe the band ($B^3\Pi_g$, $v' = 26 \rightarrow A^3\Sigma_u^+$, $v = 20$) by immersing the tube in liquid nitrogen [44]. The Y system ($^3\Sigma_u^- \leftarrow B^3\Pi_g$) has also been observed in the emission spectra at low temperatures [45]. The concentration of $N_2(B^3\Pi_g)$ in active nitrogen should be low, since the emission lifetime of this state is small, of the order of 10^{-6} s. [46]

The second positive system of nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$), which proves the presence of electronically excited $N_2(C^3\Pi_u)$ molecules in active nitrogen, can be observed only in the early stages of the afterglow, and its intensity is very low [30]. In this instance $N_2(C^3\Pi_u)$ is apparently formed in the discharge. The authors cited consider that formation of these molecules in the afterglow by $N(^4S) + N(^2D)$ collisions was observed when active nitrogen was cooled to liquid nitrogen temperature [47].

The emission of L–B–H bands ($a^1\Pi_g \rightarrow X^1\Sigma_g^+$), whose intensity is much less than that of the first positive system, was observed in the far ultraviolet [10]. Thus $N_2(a^1\Pi_g)$ molecules are present in active nitrogen in very small quantities. Mass-spectrometric methods have confirmed that active nitrogen contains highly excited electronic states of molecular nitrogen (probably $a^1\Pi_g$ or $a'^1\Sigma_u^-$, with energies of 8.548 eV and 8.398 eV respectively), but these states could be observed in quantities comparable with the concentrations of $N_2(A^3\Sigma_u^+)$ only within time intervals less than 1×10^{-3} s after the active nitrogen had left the discharge [20,33].

The presence of excited molecules in active nitrogen is revealed chemically: (1) in the decomposition of NH_3 [22,35,48–59] (nitrogen atoms doe not react with NH_3 [52,55]); (2) in the decomposition of nitric oxide to an extent greater than that corresponding to reaction (1) [51,60]; and (3) in the existence of a low-temperature (< 150°C) mechanism of the reaction of hydrocarbons with active nitrogen, differing from the high-temperature mechanism (> 150°C) [57,59]. The states of the excited nitrogen molecules responsible for these effects have not yet been identified. It has merely been established that NH_3 and hydrocarbons apparently react with the same excited nitrogen molecules, since the addition of NH_3 decreases the yield of HCN in the reaction of active nitrogen with hydrocarbons [57]. It has also been shown that NH_3 and NO react with N_2^* species in different excited states, since competition between them is not observed in their reaction with active nitrogen [51]. Herron [22] confirmed this conclusion and showed that NH_3 reacts with electronically excited metastable N_2 molecules, which can be observed by mass-spectrometric methods. Since the emission lifetime of the N_2^* species reacting with NH_3 is large (apparently much greater than 0.1 s [35,51,56]), it may be assumed that these are $N_2(A^3\Sigma_u^+)$ molecules.

To summarise, it may be concluded that active nitrogen, 0.1 s after its removal from the discharge, contains appreciable quantities of $N(^4S)$ atoms and vibrationally-excited $N_2(X^1\Sigma_g^+, v = 1)$ molecules, together with a small quantity of electronically-excited molecules, apparently in the $A^3\Sigma_u^+$ state. It is usually this active nitrogen which is used to study its chemical reactions with organic molecules. It has now been established that atomic nitrogen is the chief chemical reagent in active nitrogen [51,61–63].

The reactions of active nitrogen with organic molecules have now been studied for a long time, beginning with the work of Strutt (1911). The general features of the procedures used in these studies can be described as follows. Active nitrogen is prepared in a discharge at a nitrogen pressure of several mmHg, produced in a discharge tube by various methods. A condensed discharge, microwave discharge, or ultrahigh frequency discharge is usually employed. At atmospheric pressure active nitrogen is obtained by means of ozonisers. A current of nitrogen activated in this way is withdrawn from the discharge tube and passed into the reaction vessel. The organic compound is introduced into the same reaction vessel and reacts with the active nitrogen. The products formed are frozen out in traps and studied by chemical and physicochemical methods. The most extensive studies of the reactions of active nitrogen with organic molecules have been carried out by Winkler and coworkers. In 1956 they summarised the result of approximately ten years of work in this field [63]. The main conclusions can be summarised as follows: in the majority of reactions of active nitrogen with saturated and unsaturated hydrocarbons, alkyl chlorides, alkyl cyanides, and alkylamines, the chief and sometimes the only nitrogen-containing product is HCN; a characteristic feature of the reaction with unsaturated hydrocarbons is the formation of a nitrogen-containing polymer and a small quantity of C_2N_2; under certain conditions, all the N atoms are used up in reactions with the organic molecules. The range of studies of the chemical reactions of organic compounds with active nitrogen has now broadened considerably. A number of qualitatively new results have been obtained (some of these have been examined in a review by Mannella [64]); the most important of these results is the production of new nitrogen-containing compounds—NH_3 and various nitriles—in appreciable yield. Table 1 gives all the organic compounds whose reactions with active nitrogen have been studied, together with the reaction products. The plus sign indicates the products observed in the reaction between active nitrogen and the organic molecules listed on the left-hand side of the Table. As before, a common feature of these reactions is the formation of HCN, usually in highest yield. The preferential formation of CH_3CN in the reaction of active nitrogen with propene, observed by Lichtin [65], has not yet been confirmed [66]. Other charac-

teristic products are cyanogen and a nitrogen-containing polymer. Here, to supplement the earlier summary[63], it may be noted that the formation of a nitrogen-containing polymer and a certain amount of cyanogen is characteristic not only of unsaturated compounds, but also of halogenated hydrocarbons. The formation of a solid polymer is often observed with other organic compounds. Up to 65% of the nitrogen reacting goes into this deposit, depending on the specific system. The composition of the deposit depends on the nature of the organic compound reacting with active nitrogen: the concentration of nitrogen in the deposits obtained by various workers[77,78,82,84,87,96] varied from 16% to 37%. The polymer formed in the reaction with acetylene has been shown to have a formula of the type[90]:

$$\begin{matrix} -CH- \\ | \\ CN \end{matrix} (CH=CH)_n \begin{matrix} -CH- \\ | \\ CN \end{matrix} .$$

In the reaction with buta-1,3-diene, the deposit has the formula $(C_4H_6N)_x$,[84] and the reaction with isoprene gives the polymer $(C_3H_5N)_x$.[88] The deposit formed in the reactions with halogen-substituted hydrocarbons contains the halogen[99], and the products of the reactions with silanes have been found to contain Si–N and Si–C bonds[75]. Some experimental results indicate that the deposit is not an individual chemical compound, but a mixture[84,88,97]. Aronovich and Mikhailov[77,78] reported that the nitrogen in the deposit which they obtained is almost completely hydrolysed to NH_3. The ease of hydrolysis suggested to them that the deposit contained nitrile or even imino-groups. The chemical inertness of these deposits makes their study difficult.

TABLE 1. Nitrogen-containing products of the reactions of atomic nitrogen with organic compounds*.

Original organic compounds	Nitrogen-containing products of the reactions: HCN	$(CN)_2$	nitrogen-containing polymer	NH_3	ClCN	CH_3CN	C_2H_5CN	References
Methane	+			+		+		57,66–69
Ethane	+		+	+				51,57,59,63, 66,67,70
Propane	+							59,63,72
Cyclopropane	+							63,73
n-Butane	+			+				51,63,74
Isobutane	+							63,74
Cyclobutane	+							63
Neopentane	+			+				59,67,73,75, 76
Cyclopentane	+							73
n-Hexane	+		+	+				75,77,78
Cyclohexane	+		+	+				75,77,78
n-Hexadecane	+	+		+		+		79
Ethylene	+	+	+	+				23,51,63,69, 70,71,80,81
Propene	+	+	+			+	+	63,65,71,82
But-1-ene	+							63,83
But-2-ene	+			+				51,63,83
2-Methylpropene	+							63,83
Buta-1,3-diene	+	+	+			+	+	84,86
Isoprene	+		+	+				85,87,88
Cyclohexene	+		+					77,78
Benzene	+		+	+				75,77,78
Benzonitrile	+		+					87
Naphthalene	+		+					77,78
Tetralin	+		+					87
Acetylene	+	+	+					63,70,71, 90–94
Methylacetylene	+	+	+					71,92–94
Dimethylacetylene	+	+						92
Diphenylacetylene	+		+					87
Methanol	+					+		68,95
Ethanol	+					+	+	68,96
Propan-2-ol	+							96
Benzaldehyde	+		+					77,78
Cyclohexanone	+		+					77,78
Acetic acid	+		+					77,78
Stearic acid	+		+					77,78
Oleic acid	+		+					77,78
Butyl oleate	+		+					77,78
Dibutyl phthalate	+		+					77,78
Carbon tetrachloride			+		+			89,97,98
Chloroform	+	+	+		+			97,98
Methylene chloride	+	+	+		+			97
Methyl chloride	+	+	+		+			98,99
Methyl bromide	+		+					98
Chloroethane	+	+	+					99
1-Chloropropane	+	+	+					99
2-Chloropropane	+	+	+					99
Chloroethylene	+	+	+					99

TABLE 1 (contd.)

Original organic compounds	Nitrogen-containing products of the reactions: HCN	$(CN)_2$	nitrogen containing polymer	NH_3	ClCN	CH_3CN	C_2H_5CN	References
Methylsilane	+			+				100
Dimethylsilane	+			+				100
Trimethylsilane	+			+				100
Tetramethylsilane	+		+	+				75,100
Siloxane heptamer	+			+				79
Polyethylene	+	+						101
Polypropylene	+	+		+				101
Poly-2-methylpropene	+	+		+				101
Methyl cyanide	+							92–94
Azomethane	+							102
Methylamine	+			+				75,92–94
Ethylamine	+			+				75

* The following products have also been found in reactions of atomic nitrogen: with buta-1,3-diene—1-cyanobuta-1,3-diene, 3-cyanobutadiene, 3-cyanobut-1-ene, 1-cyanopent-3-ene, crotonitrile, and pyrrole; with isoprene—crotonitrile, pyrrole, and β-methylpyrrole; with benzene—benzonitrile, phenyl isocyanide, and pyridine; with naphthalene—quinoline and isoquinoline; and with cyclohexanone—cyanohydrins.

It can be seen from Table 1 that there are a large number of compounds which react with active nitrogen to give ammonia and nitriles; the formation of NH_3 is characteristic of alkanes, methyl-substituted silanes, and polymers containing methyl groups, and the formation of nitriles is characteristic of alkenes and halogenated methanes. A distinctive feature of the reactions of the latter is the formation of ClCN. Ammonia is extremely convenient both for direct use and for subsequent conversion into valuable nitrogen-containing products, so that its formation in the reactions of active nitrogen with organic compounds is of particular interest. Unfortunately, the absolute yield of NH_3 is generally low: for hydrocarbons[70] and siloxane[79], it does not exceed 10 mole %, calculated on the organic reagent decomposed. The yield of NH_3 for methylsilanes is much greater, but the reaction rate is smaller by one order of magnitude than that for hydrocarbons[75]. In all instances the yield of NH_3 is lower than the yield of HCN. The appropriate data (Table 2) show that in the reactions of active nitrogen with hydrocarbons, the yield of NH_3 is usually 10–20% of the yield of HCN. Winkler and coworkers[57] showed, however, that this figure can be increased to 50% by increasing the flow rate of the organic reagent. It should be noted that the latter reaction was carried out below 150°C. There are thus grounds for assuming that excited nitrogen molecules play an important part in altering the mode of the reaction. For organosilicon compounds, a change in the NH_3/HCN ratio with change in temperature was not observed[79,100]. The

TABLE 2. Maximal values of the relative yield of NH_3 obtained in reactions of organic compounds with active nitrogen.

Organic compound	NH_3/HCN, %	References	Organic compound	NH_3/HCN, %	References
Methane	50	57	Methylsilane	2	100
Ethane	16—20	51,70	Dimethylsilane	20—30	100
	50	57	Trimethylsilane	30—40	100
Butane	16	96	Tetramethylsilane	40—50	75,100
Neopentane	20	75	Siloxane heptamer	48	79
Hexane	20	75	Polypropylene	46	101
Cyclohexane	12	75	Poly-2-methylpropene	21	101
n-Hexadecane	10	79	Ethylamine	65	75
Ethylene	15	51,70	Methylamine	89	75
But-2-ene	16	51			
Benzene	18	75			

absolute and relative yields of NH_3 increase with increase in the concentration of methyl groups in the original molecule[88,100,101].

Despite extensive study of the reactions of active nitrogen with organic compounds, few results have indicated the possibility of forming products corresponding to the mild degradation of the original organic molecules in appreciable yield in these reactions. It is these data, however, which throw light on the mechanism of the reaction of active nitrogen with organic molecules. The formation of benzonitrile[77,78,87] and pyridine[77,78] in the reaction of active nitrogen with benzene, and the formation of quinoline and isoquinoline in the reaction with naphthalene[77,78] are of interest in this connection. Work by Lichtin and coworkers[84-86], specially undertaken to find conditions for obtaining products of the mild degradation of the original molecules, showed that a large number of nitriles and pyrrole are formed in the reactions of buta-1,3-diene and isoprene with active nitrogen.

The reactions of active nitrogen with organic molecules are usually very rapid. The kinetic characteristics of a number of reactions are given in Table 3. Most of the kinetic data relate to the overall reactions of HCN formation. In some instances it has been assumed[23,58,95,103,105] that the initial attack by the N atom on the organic molecule is the rate-determining step in the complex reaction of HCN formation, and the kinetic constants obtained by the authors cited relate to the corresponding fundamental reaction. This assumption is based on the view that the subsequent stages leading to the formation of HCN involve organic radicals, and therefore should take place very rapidly. The problem of assigning the experimentally determined effective rate constants to given fundamental reactions can be resolved, however, only after the complete reaction mechanism has been established. Such studies have not yet been carried out for any reaction of active nitrogen with an organic molecule. In the reactions studied the systems always contain atomic hydrogen[23,63], which produces radicals by reacting with the organic molecules; from the kinetic viewpoint this may lead to appreciable "masking" of the initial step in the formation of HCN from atomic nitrogen and the organic molecule. Most kinetic studies of the reactions of active nitrogen with organic molecules have been carried out in low-pressure flow systems. The dependence of the yield of HCN on the concentration of the reagents and temperature, or on the duration of the reaction and temperature, has been studied. The results have been analysed on the assumption that the

TABLE 3. Kinetic constants for the reactions of active nitrogen with various organic molecules*.

Organic molecule	Temperature, °K	A, $cm^3 mole^{-1} s^{-1}$	P		E, kcal $mole^{-1}$		k, $cm^3 mole^{-1} s^{-1}$	Refs.
			laminar	turbulent	laminar	turbulent		
Methane	313—773		10^{-2}—10^{-3}		11—13			63,66,67
Ethane	380—500		3×10^{-3}	7×10^{-2}	6.2	7.9		63,66,67
	423—748		6.4×10^{-4}	2×10^{-3}	5.7	6.3		63,65
	173—423		1.4×10^{-5}	1.2×10^{-5}	2.7	2.4		63,65
	278—423	8.7×10^{-15}	2×10^{-5}		1.7			59
	423—703	3.8×10^{-12}	6×10^{-3}		7			59
Propane	278—703	8.7×10^{-12}	1.9×10^{-2}		5.5			59
	336—523		9.1×10^{-4}	2.1×10^{-2}	5.1	6.2		63,72
Butane	75—250		4.5×10^{-4}		3.6			63,74
Isobutane	100—260		4.4×10^{-4}		3.1			63,67
Neopentane	233—423		1.1×10^{-6}	3.3×10^{-5}	2.0	2.0		63,67
	423—623		2.7×10^{-4}	4.9×10^{-2}	6.5	7.7		63,67
	278—423	4.8×10^{-15}	1.0×10^{-5}		1.5			59
	423—703	2.3×10^{-12}	3.4×10^{-3}		6.6			59
Cyclopropane	—		1.9×10^{-5}	5×10^{-4}	3.2	4.0		63
Cyclobutane	—		1.5×10^{-4}	4.1×10^{-2}	4.6	6.4		63
Ethylene	310		10^{-5}				1.6×10^{-13}	
	295—673		10^{-5}		0.4±0.2		1.7×10^{-14} at I=295°K	103,104
	473—603				<1		9.6×10^{-14} at I=500°K	105
	320				>1		1.2×10^{-14}	
	291—523	$1.2\times10^{-14}/\sqrt{T}$			1.5±0.2		2×10^{-14} at I=320°K	23,80
	325						6.6×10^{-14}	
	423						3×10^{-14}	81
Acetylene	70—90				0.25			58
	291—523	$9.35\times10^{-16}/\sqrt{T}$			2.3±0.2			90
Polyethylene	312—419				1.7±0.7			91
Methanol	303—755		2.3×10^{-3}	3.7×10^{-3}	3.4	3.7		101
Ethanol	300—593		3.6×10^{-3}		3.4			95
Propan-2-ol	300—593		3.8×10^{-3}		3.5			96
Azomethane	323—673		10^{-2}—10^{-4}		1.9±0.3			96
Methyl radical	323—673		10^{-1}—10^{-3}		0.5±0.4			102
								102

* Symbols used in the table: A is the pre-exponential term in the expression for the reaction rate constant $k = A\exp(-E/RT)$, P the steric factor, E the activation energy, and k the reaction rate constant.

only chemically active species in the active nitrogen are nitrogen atoms, and that their reactions with organic molecules are bimolecular. For comparatively slow reactions, the calculations of the kinetic constants in a number of instances were carried out assuming both laminar flow and turbulent flow of active nitrogen in the reaction vessel. The methods generally used to determine the concentration of nitrogen atoms are as follows: (a) titration of the stream of active nitrogen with nitric oxide, based on reaction (1); and (b) determination of the maximal yield of HCN in the reaction of active nitrogen with ethylene. The values obtained for the concentration of nitrogen atoms by the first method are on the average one and a half times those obtained by the second method. Until recently it was not clear which method ought to be given preference, so that both were used. Only recently it was shown convincingly[23] that the reaction with ethylene involves recombination of nitrogen atoms, catalysed by intermediate products, so that preference must be given to the reaction with nitric oxide. The kinetic constants obtained by using NO to determine the concentration of nitrogen atoms can therefore be regarded as more reliable.

A second serious source of errors lies in the determination of the reaction time. It is necessary to be able to stop the reaction sharply at a given moment of time, and this is a difficult task in reactions of active nitrogen with organic molecules, particularly reactions with unsaturated compounds, which take place extremely rapidly. Comparison of a number of methods [104] has shown that two are most suitable for this purpose: (1) a method based on the introduction into the reaction zone of NO, which stops the reaction by reacting rapidly with the remaining nitrogen atoms; and (2) the removal of nitrogen atoms from the reaction by rapid surface recombination on a cobalt catalyst. The mean values of the reaction rate constants obtained using the two methods show good agreement [104].

There are a number of other sources of systematic errors in the flow method for studying the kinetics of the reactions of active nitrogen with organic molecules. For example, allowance is not always made for the following factors: deactivation of N atoms within and on the surface of the reaction vessel (flow tube), the influence of the reaction on the pressure gradient in the flow tube and on the rate of flow, the influence of impurities formed by erosion of the electrodes in the discharge tube, and the influence of hydrogen atoms. Thus the kinetic constants obtained in early work must be regarded merely as estimates of the appropriate quantities, to within one order of magnitude. It must also be borne in mind that the data given in Table 3 are influenced by errors associated with imprecise knowledge of the reaction mechanisms. To estimate the magnitude of these errors, it may be noted that the individual values of the rate constants for the reactions of active nitrogen, determined using improved methods, deviate from their arithmetic mean by 10–25% within the ranges of reagent concentration and duration of reaction studied. A regular increase in the rate constants with decrease in the duration of the reaction is observed, indicating the complexity of the process and hence the relative value of the arithmetic-mean rate constants for the reaction of active nitrogen. The reactions of active nitrogen with ethylene have been the subject of the greatest number of kinetic studies, because of the unique part played by this reaction in the study of active nitrogen. The method of diffusion flames [81,103] has been used to obtain approximate values of the rate constant for this reaction. More reliable values were obtained in work [23,104] in which the results were analysed by various methods, and the values obtained for the constants showed good agreement. The most reliable value of the rate constant for the first fundamental step in the reaction of active nitrogen with ethylene,

$$N + C_2H_4 \rightarrow HCN + CH_3 . \qquad (6)$$

is that obtained by Herron [23]. This determination was based on a precise knowledge of the reaction mechanism. Other rate constants [80,100] assigned to stage (6) are slightly higher than those given by Herron. These constants [80,100] apparently cannot be assigned to this fundamental reaction step, and they should rather be regarded as more accurate values of the rate constant for the overall reaction of HCN formation.

The mechanism of the reaction of active nitrogen with organic molecules has not yet been elucidated. In accordance with the unified mechanism proposed by Winkler for these reactions, it is assumed that the nitrogen atoms attack directly one of the carbon atoms in the organic molecule, and that the resulting complex decomposes according to a unimolecular law with the formation of HCN as the product of the primary stage of the reaction, together with organic radicals, which subsequently react rapidly with atoms, again with the formation of HCN. For example, the formation of HCN from propane, propene, propyl chloride, and ethanol can be represented as follows:

$$N + C_3H_8 \rightarrow [NC_3H_8] + H_2 \rightarrow HCN + C_2H_5 + H_2 \qquad (7)$$

$$N + C_3H_6 \rightarrow [NC_3H_6] \rightarrow HCN + C_2H_5 \qquad (8)$$

$$N + C_3H_7Cl \rightarrow [NC_3H_6] + HCl \rightarrow HCN + C_2H_5 + HCl \qquad (9)$$

$$N + C_2H_5OH \rightarrow [NC_2H_5] + OH \rightarrow HCN + CH_3 + OH . \qquad (10)$$

Winkler's mechanism provides a satisfactory explanation for the formation of not only HCN but also new hydrocarbons and other compounds which do not contain nitrogen. In the selection of probable reactions it is necessary only to make allowance for energy and spin restrictions [63]. For reasons related to the energetics of the process, however, it is doubtful if this mechanism is applicable to the reactions of lower hydrocarbons. It has also been shown that that hydrocarbon radicals play an important part in the reactions of hydrocarbons with active nitrogen [106]. Safraniy et al. [106] consider that the lower alkanes must first form radicals, which then react rapidly with N atoms to form HCN. The initial formation of radicals from alkanes is an unresolved problem. It is possible that the excited nitrogen molecules which are present in active nitrogen may act as initiators in these reactions. All that has been said above relates to the mechanism of HCN formation. The formation of NH_3 and the various products obtained by mild degradation of the organic molecules also requires explanation. For example, the pyrrole and *trans*-crotonitrile obtained by the reaction of active nitrogen with buta-1,3-diene can be regarded as the products of the attachment of an N atom to the original molecule and the removal of an H atom. The mechanism of this substitution is not yet clear. Ammonia may be formed by the reactions of N atoms with molecular or atomic hydrogen, produced by the decomposition of the organic reagents with active nitrogen. This was used, in particular, to explain the formation of NH_3 in the reactions of active nitrogen with ethane and ethylene frozen at −196°C. [70] In general, however, this explanation cannot be regarded as satisfactory, as there are a number of serious objections. The formation of NH_3 in a reaction with atomic hydrogen should pass through a stage involving the formation of an NH radical, which decomposes very readily:

$$NH + NH \rightarrow N_2 + H_2 \qquad (11)$$

$$NH + N \rightarrow N_2 + H . \qquad (12)$$

The NH_2 radical, which is the intermediate species in the formation of NH_3 by the reaction of atomic nitrogen with molecular hydrogen, decomposes in analogous fashion:

$$NH_2 + N \rightarrow N_2 + H_2 . \qquad (13)$$

Thus the intermediate species produced in the formation of ammonia not only disappear themselves in side reactions which take place readily, but also lead to the irreversible removal of the original reagent—N atoms—from the reaction. The decomposition of NH and NH_2 radicals should evidently be particularly efficient in an excess of nitrogen atoms, and this is usually the situation in the reactions of active nitrogen with organic compounds. Moreover, the reaction of N with H_2 is termolecular [107]:

$$N + H_2 + N_2 \rightarrow NH_2 + N_2 \qquad (14)$$

and its rate is therefore low ($k = 0.85 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}). It can be observed only at pressures of molecular nitrogen greater than 6 mmHg. [107] The formation of NH_3 is always observed, however, at pressures below

6 mmHg. Thus the formation of NH_3 under the conditions of the reactions of active nitrogen with organic molecules apparently does not take place in secondary reactions of the N atoms with hydrogen liberated by the decomposition of the original organic molecules. The correlation between the formation of NH_3 and the number of methyl groups in the original organic molecule suggests that NH_3 is formed in a single stage in some process in which the N atom displaces two or three H atoms from the CH_3 group[75,89,100].

The reactions of hot N atoms, formed in the process $^{12}C(d, n)^{13}N$, with organic molecules also leads to the formation of chiefly HCN with a small quantity of nitriles[68,69,89,98]. Thermalisation of the ^{13}N atoms does not alter significantly the composition and yield of the products[69]. As in the reactions of active nitrogen, CN radicals do not play a significant part in the formation of the products[69]. Thus the reactions of hot N atoms with organic molecules resemble the reactions of active nitrogen. The mechanism of these reactions is identified with Winkler's unified mechanism, which in this instance is applicable even to the lower alkanes, if it is postulated that the reacting species are excited $N(^2D)$ atoms[69]. An interesting feature is that it has been proved that in systems of this type organic radicals do not influence the reaction rate[68] and that the addition of nitric oxide had little influence on the yield of HCN[69].

3. REACTIONS OF EXCITED NITROGEN MOLECULES

The electronic excitation of a molecule generally makes it more reactive. This is due to a number of factors[108]: (1) on excitation, unpairing of one of the electron pairs of the molecule takes place, facilitating the attachment of another molecule with an unpaired electron; (2) the excited electron is less firmly held by the molecule, so that the reaction of the excited molecule with an electrophilic reagent is facilitated; and (3) the excited electrons sometimes play little part in chemical bonding, so that the energy required for dissociation of the molecule is decreased. It is known[109], however, that simple excited molecules are very rarely the initial centres of chemical reactions. We should therefore not expect reactions of excited nitrogen molecules with organic molecules to be very widespread. This problem has been insufficiently studied by experiment. Photochemical study of nitrogen is difficult, since N_2 absorbs light only with $\lambda < 1450$ Å (8.546 eV) and its absorption cross-section in the $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ bands is less than 4×10^{-21} cm^2.[110] Thus information on the reactions of excited nitrogen molecules is very limited and is conjectural in character, since it has been obtained indirectly, chiefly in the study of the reactions of active nitrogen. Direct photo-activation of a mixture of nitrogen and methane at a pressure of 5–8 mmHg was achieved by Dodonova[111]. Light from a hydrogen lamp with $\lambda > 1250$ Å and intensity 10^{15}–10^{16} photon s^{-1} was used for the photo-activation. The formation of HCN was detected under these conditions.

Study of the reactions of active nitrogen with hydrocarbons has revealed facts whose explanation required the assumption that active nitrogen contains excited N_2^* molecules, which react with organic molecules[34,38,52,112]. It has been proved that the N_2^* molecules react with CH_4,[57] C_2H_6,[51,57,59] $C(CH_3)_4$,[59] C_2H_4,[51] and CCl_4.[49] Since the conditions under which the reactions take place with the participation of N_2^* give the same products as the conditions under which the chief reagent is atomic nitrogen, it is assumed that second-order collisions with N_2^* molecules excite organic molecules; these subsequently dissociate to form radicals, which react with atomic nitrogen in the usual way[51,59]. The reaction mechanism can then be represented as follows:

$$N_2^* + RH \rightarrow N_2 + RH^* \quad (15)$$

$$RH^* \rightarrow R + H \quad (16)$$

$$R + N \rightarrow HCN \text{ and other products} . \quad (17)$$

It is apparently possible that in a number of instances the participation of N_2^* in reactions with organic molecules may alter the mode of these reactions. Thus in the reaction of active nitrogen with CH_4, C_2H_6, and C_2H_4 below 150°C a considerable increase in the yield of NH_3 compared with the yield of HCN has been observed[51,57]. This was attributed to the participation of nitrogen in excited-molecule reactions[51]. The excited state of N_2^* reacting with hydrocarbons has not been reliably identified. It is usually assumed, however, that long-lived excited states of the molecules are most important in chemical reactions. Table 4, taken from a paper by Phillips[113], gives the long-lived states of molecular nitrogen. Of these, $A^3\Sigma_u^+$, $^3\Delta_u$, and $a^1\Pi_g$ have been detected in the afterglow of nitrogen, and the $^5\Sigma_g^+$ state has been postulated[64]. No definite proof has been obtained for the presence of the $^3\Delta_u$ state in active nitrogen; it was selected as the upper state of the so-called Y series recently discovered in the afterglow of nitrogen[45,114]. Here a choice was made between the $^3\Delta_u$ and $^3\Sigma_u^-$ states. Later results[115] indicated that the upper state in this series is more likely to be $^3\Sigma_u^-$ than $^3\Delta_u$. If $N_2(^3\Delta_u)$ molecules are present in active nitrogen, their concentration should be very low, since this state is apparently readily deactivated in collisions with nitrogen molecules in the ground state[116]. Thus the part played by $N_2(^3\Delta_u)$ in the reactions of active nitrogen with organic molecules cannot be important.

Nothing definite can be said regarding the part played by the excited $^5\Sigma_g^+$ state, since there are no experimental data. Estimates of the lifetime of N_2^* molecules reacting with organic molecules[35,51] gave values slightly greater than $\tau_{emission}$ for the $a^1\Pi_g$ state, excluding the possibility that this state takes part in the reactions with hydrocarbons. The properties of $N_2(A^3\Sigma_u^+)$ molecules, however (the long lifetime, the difficulties associated with the transfer of energy to nitrogen molecules in the ground

TABLE 4. Long-lived states of molecular nitrogen*.

State	Energy ($v = 0$), kcal mole^{-1}	D^0, kcal mole^{-1}	$\tau^*_{emission}$, s	References
$X^1\Sigma_g^+$	0	225	—	
$A^3\Sigma_u^+$	142	83	2.6×10^{-2}	39
			1	13,36,119–121
			0.2–50	122
			12 ± 2.4	123
$^3\Delta_u$	[172]	[107]	1–2	124,125
$a^1\Pi_g$	196	138	1.7×10^{-4}	38,39
$a'^1\Sigma_u^-$	(202)	(132)	4×10^{-2}	39
$^5\Sigma_g^+$	(222)	(3)		
$[^1\Sigma_g^+]$	[(280)]	[(182)]		

* Predicted states or values are given in square brackets, doubtful values are given in parentheses, and the asterisk at the lifetime values indicates that they were introduced into the table by the author.

state [13], and their ready deactivation in collisions with impurities [81,117], make their participation in the reactions of active nitrogen with organic molecules extremely probable, as suggested by Winkler and coworkers [57]. This is confirmed by the competition between the reactions of hydrocarbons and ammonia with active nitrogen [49,51,57], since we now have a considerable amount of evidence that the $A^3\Sigma_u^+$ state of molecular nitrogen is responsible for the decomposition of ammonia in active nitrogen [35]. Safrany et al. [106,118] cast doubt on the initiating role of $N_2(A^3\Sigma_u^+)$ molecules in the reactions of active nitrogen both with organic molecules and with NH_3. They showed, in particular, that an increase of the concentration of $N_2(A^3\Sigma_u^+)$ in active nitrogen as a result of the recombination of N atoms catalysed by a metal surface does not alter the rate of decomposition of hydrocarbons and NH_3. [106,118] The decomposition of ammonia by paramagnetic non-atomic species present in active nitrogen has been confirmed, however [35]. The authors cited consider that these species are $N_2(A^3\Sigma_u^+)$ molecules. There are thus a number of indications that it is the $N_2(A^3\Sigma_u^+)$ species which reacts with organic molecules.

TABLE 5. Types of reaction of nitrogen ions with organic molecules.

Reaction No.	Reaction	Energy of ions, eV	Type of reaction	Refs.
1	$N_2^+ + CH_4$	1000	Dissociative charge transfer	127,128
2	$N_2^+ + CD_4 \rightarrow N_2D^+ + CD_3$	—	Transfer of heavy species	129
3	$N_2^+ + C_2H_6 \rightarrow N^+ + N + C_2H_6$	5000	Dissociation induced by collision	130
4	$N_2^+ + C_2H_4 \rightarrow N^+ + N + C_2H_4$	5000	ditto	130
5	N_2^+ + aromatic compounds	7—500	Dissociative charge transfer	127
6	$N_2^+ + CH_3COOCH_3$	110—150	ditto	131
7	$N_2^+ + CCl_4$	14—150	Transfer of heavy species and molecular rearrangement	132
		150—200	Dissociative charge transfer	132
8	$N_2^{2+} + CCl_4$	3—200	ditto	132
9	$N^+ + CH_4$	5000	»	133
10	$N^+ + CCl_4$	3—30	Transfer of heavy species and molecular rearrangement	89,132
		30—200	Dissociative charge transfer	89,132
11	$N^+ + CF_4$	3—200	ditto	89
12	$N^+ + CF_3Cl$	3—200	»	89

4. REACTIONS OF NITROGEN IONS

a. Positively charged ions. The ion-molecule reactions of compounds of various classes are now being studied extremely intensively. Data on the ion-molecule reactions of nitrogen with organic molecules are still limited, however. There is published information on the reactions of N_2^+, N_2^{2+}, and N^+ ions with organic compounds of various classes: alkanes (CH_4, C_2H_6), alkenes (C_2H_4), aromatic compounds [C_6H_6, $C_6H_5CH_3$, $C_6H_5CH(CH_3)_2$], ketones (CH_3COCH_3), and halogen-substituted alkanes (CCl_4, CF_4, CF_3Cl). All these studies have been carried out in mass-spectrometer ion sources. All the above reactions, except the reaction with CD_4, [129] were studied by bombarding the organic molecules in the gaseous phase with nitrogen ions obtained in a separate ion source: the reaction with deuteriomethane, however, was carried out in an ionisation chamber, in which a mixture of deuteriomethane and nitrogen was ionised with fast electrons, and the reactions of the ions formed were studied. In other words, the methods used were those of external and internal ionisation, using the nomenclature proposed by Tal'roze [126].

Dissociative charge transfer or ion dissociation processes, induced by collision, are most characteristic of the reactions of positive nitrogen ions with organic molecules in the ranges of ion energies studied (see Table 5). Dissociative charge transfer gives a spectrum of organic fragment ions, and there is a tendency for the ions formed in greatest yield to be those which best satisfy the requirements of the resonance principle, that is the ion whose formation is most intensive is the one for which the absolute magnitude of the heat of formation Q is minimal [$Q \simeq$ (energy of recombination of the primary ion with an electron) – (appearance potential of the fragment ion)] [128]. Superimposed on this tendency, however, is the requirement that the corresponding fundamental reaction be exothermic [128]. Both of these requirements reflect the general laws governing ion – molecule reactions of this type [138].

Transfer of heavy species has been observed only in three instances (reactions 2, 7, and 10 in Table 5), where formation of the ions N_2D^+, NCl^+, $NCCl^+$, and NC^+ was observed; it may also be assumed that in reaction 6 some ions also contain nitrogen. In the last instance, however, not all the ions in the resultant mass spectrum were identified, and insufficient justification was obtained for the suggestion put forward. Evidence in support of the suggestion is provided by the following considerations: some of the fragments do not fit into the scheme proposed by the authors cited to explain the mass spectrum, and the molecular weights of these fragments suggest that they contain nitrogen; for example, the value $m/e = 29$ may correspond to the N_2H^+ ion. A small quantity of N_2H^+ ions was also observed in reactions 5. The intensity of the nitrogen-containing ions in this instance, however, was low compared with the ions resulting from charge transfer. The kinetics of the reactions of nitrogen ions with organic molecules have not been studied. The single exception is the reaction

$$N_2^+ + CD_4 \rightarrow N_2D^+ + CD_3 \qquad (18)$$

for which the cross-section is found to be about 4×10^{-16} cm^2 molecule^{-1} ($k \simeq 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [88]. The studies which have been carried out are as yet insufficient to enable any conclusions to be reached regarding the part played by ion-molecule reactions in the formation of nitrogen-containing organic products during radiolysis. The available data indicate, however, that the formation of nitrogen-containing fragment ions depends both on the energy of the ions and on the chemical nature of the molecules and ions. It may therefore be expected that there exist systems or conditions, in which ion-molecule exchange reactions between nitrogen and organic molecules take place to a significant extent. The absence of such processes in most of the reactions studied can be attributed, for example, to the fact that the studies were carried out using ions whose kinetic energies were too large, whereas the transfer of heavy species in ion-molecule reactions most probably takes place at low energies [138].

b. Negatively charged nitrogen ions. The negative nitrogen ions N^- and N_2^- have not been detected in the ground state, due to the very low electron affinity of both atomic and molecular nitrogen. The formation of an N^- ion in the excited state by the attachment of an electron to an excited nitrogen atom is possible [134-136]. The excited

$N^-(^1D)$ and $N^-(^1S)$ states are metastable, but their possible breakdown as a result of self-ionisation often hinders even the experimental detection of these ions[95]. Accordingly, ion-molecule reactions with the participation of negative nitrogen ions are unknown.

The azide ion N_3^-, formed by the dissociation of NaN_3, exists in solutions. If undergoes photochemical reactions fairly readily; for example, it reacts with water with the formation of N_2, NH_2OH, N_2H_4, and NH_3 on irradiation by light with $\lambda = 2540$ Å,[137] but as yet nothing is known of its reactions with organic molecules.

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ADVANCES IN THE CHEMISTRY OF THE TROPYLIUM ION

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I. INTRODUCTION

The tropylium cation, predicted in 1931 by Hückel[1] and obtained in 1954 by Doering and Knox[2], constitutes a non-benzenoid aromatic system. According to Vol'pin's definition, "those unsaturated cyclic compounds are aromatic in which all the atoms in the ring are involved in the formation of a single conjugated system, the π-electrons of the system forming a closed† electron shell"[3].

In fact, the seven-membered tropylium ring has a sextet of π-electrons, like benzene and the cyclopentadienyl anion, i.e. it obeys Hückel's rule. Calculation shows that the six π-electrons of the tropylium ion are distributed among the bonding molecular orbitals and form a closed electron shell; the removal and addition of electrons increase the total energy of the system, lowering its stability. The planar structure of the ions follows from X-ray diffraction data[4]. The identity of all seven carbon atoms in the tropylium ion and hence the equality of all the carbon–carbon bonds in the ring have been demonstrated by the radioactive tracer method[5]. The high degree of symmetry of the tropylium cation is also reflected in a small number of infrared and Raman absorption bands[2,6].

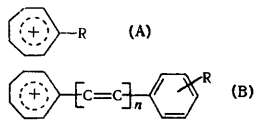
From the chemical point of view, the aromaticity of the tropylium ion is shown in the ease of its formation. The tropylium ion forms under the action of oxidising agents, including hydride ion acceptors (see p. 746), on cycloheptatriene, in the degradation of cycloheptatriene derivatives under the action of electrophilic agents (see p. 747), and when isomeric C_7H_8 hydrocarbons are subjected to electron impact in a mass spectrometer (see p. 748).

The tropylium cation is extremely stable to the action of electrophilic agents[7], exhibiting at the same time high reactivity towards nucleophilic agents[3,8]. Many examples confirming the high electrophilicity of the tropylium cation are known at the present time. Thus the cation combines with many nucleophilic agents[9]. In particular, the tropylium ion is used for the investigation of hydride migration reactions as a hydride ion acceptor[10]. It readily alkylates double bonds activated by electron donor substituents and compounds with "labile" hydrogen (see p. 749). Reactions involving nucleophilic substitution of one group by another are characteristic of the tropylium system[8,11,12]. These properties of the tropylium ion make it a splendid model for the investigation of the properties of carbonium ions, in most cases unstable, which are formed in many chemical reactions as transient intermediates.

The advances achieved in the chemistry of the tropylium ion up to 1960 have been described in Vol'pin's review[3]. In recent years the number of papers on the chemistry of the tropylium ion has increased greatly and in many of them new problems have been posed. We thought it timely to describe in detail problems which were not discussed or discussed superficially in Vol'pin's review. Chapters II, III, and IV of our review deal with these new problems in the chemistry of the tropylium ion. In Chapter V we attempted to describe briefly the papers in which the problems posed in the previous reviews have been developed and new evidence concerning them has been obtained.

II. ACIDITY OF SUBSTITUTED TROPYLIUM IONS

The stability of the tropylium ring changes on introduction of a substituent. Let us consider the effect of substituents on the stability of cations of three types:



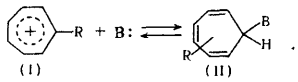
benzotropylium derivatives (C)

The pK_a values for the acid–base equilibrium

$$R^+ + 2H_2O \rightleftarrows ROH + H_3O^+$$

can serve as quantitative characteristics of the stability of carbonium ions. The higher is the pK_a of the carbonium ion the lower is its acidity and, as a rule, the higher its stability in relation to nucleophilic agents. Table 1 lists the pK_a values for the most stable carbonium ions[2,13,14].

In the study of the effect of the substituent on the acidity of the tropylium cation it is necessary to take into account the energy of the conjugation of the substituent both with the tropylium system (I) and the cycloheptatriene system (II):



(I) (II)

If the difference between the conjugation energies of the unsubstituted and substituted tropylium ion (I) is higher than the difference between the conjugation energies of the

TABLE 1.

Cation	pK_a	Cation	pK_a
Tropylium	+4.75*	Triphenylmethyl	−6.63**
Tri-p-anisylmethyl	+0.82**	Diphenylmethyl	−13.3**
Tri-p-tolylmethyl	−3.56**	Fluorenyl	−14.0**

* Measurements in water.

** Measurements in sulphuric acid.

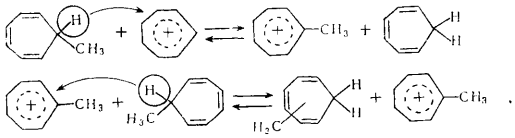
† In the sense given to this term by Hückel.

unsubstituted and substituted cycloheptatriene (II), then, other conditions being equal (change in hybridisation, entropy and solvation effects), electron-donor substituents which delocalise the positive charge of the tropylium ion will reduce its acidity, i.e. its pK_a value will increase. Electron-acceptor substituents should increase the acidity of the tropylium ion. This relation between the acidity and the electron-acceptor or electron-donor properties of substituents has been observed for cations of types (A) and (B), a larger pK_a value indicating in this case a higher stability of the substituted tropylium ion.

If the substituent has a greater effect on the cycloheptatriene system than on the tropylium system, then on introduction of electron-donor substituents delocalising the positive charge of the tropylium ion the acidity of the latter will increase, i.e. the pK_a value will fall. The introduction of electron-acceptor substituents should in this case lead to an increase of the pK_a value. An example of this type of effect of substituents on the acidity of the tropylium ion is the acidity of benzotropylium cations[15-19].

At present there are few data concerning the acidity of substituted tropylium ions of type (A). Johnson et al.[20] showed that the introduction of the electron-acceptor carboxy-group into the tropylium ring lowers the pK_a value from +4.75 for the unsubstituted tropylium ion to +3.3 for the carboxytropylium ion, i.e. reduces the stability of the cation. On the other hand, the introduction of the electron-donor methyl group enhances the stability of the tropylium ion. The acidity constant of the methyltropylium ion has not been measured. However, the stability of tropylium ions can be inferred from the free energy responsible for their reactivity.

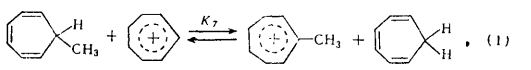
Conrow[21] showed that the free energy of the methyltropylium ion is smaller by 3.7 kcal mole^{-1} than that of the unsubstituted tropylium ion. He investigated the isomerisation of 7-methylcycloheptatriene under the action of the tropylium ion and showed that under these conditions unsubstituted cycloheptatriene forms in addition to the isomeric methylcycloheptatrienes. During a certain period the amount of cycloheptatriene remains constant and no longer changes, while the amount of 7-methylcycloheptatriene continues to decrease. These results enabled Conrow to propose the following reaction mechanism:



The tropylium ion removes a hydride ion from the 7-methylcycloheptatriene molecule with formation of cycloheptatriene and a methyltropylium ion. The latter enters into a further reversible hydride transfer reaction with methylcycloheptatriene.

To confirm this mechanism, Conrow investigated the reduction of the methyltropylium ion with lithium aluminium hydride, sodium borohydride, and calcium hydride. It was found that the relative amounts of methylcycloheptatrienes obtained in this case, where hydride transfer undoubtedly takes place, are approximately the same as in the isomerisation of 7-methylcycloheptatriene.

Knowing the relative amounts of the isomeric methylcycloheptatrienes in the reaction of the methyltropylium ion with lithium aluminium hydride, and also having determined chromatographically the yield of each isomeric methylcycloheptatriene in the isomerisation reaction, Conrow calculated the free energy of the equilibrium reaction (1),

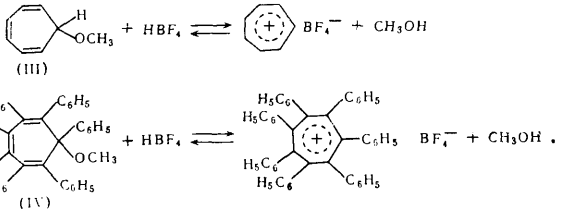


i.e. $\Delta F_7 = -3.72$ kcal mole^{-1}.

Conrow suggested that the resonance energies of 7-methylcycloheptatriene and cycloheptatriene are equal (to within not more than 0.3 kcal mole^{-1}) and their solvation conditions are the same, so that the free energy of reaction (1) can be attributed only to the difference between the free energies of the tropylium and methyltropylium ions. This difference is 3.7 kcal mole^{-1}. Having obtained this quantity, Conrow calculated the free energy differences between the isomeric methylcycloheptatrienes. It follows from his calculations that the methyl group stabilises the tropylium ion much more (by 3.7 kcal mole^{-1}) than the cycloheptatriene molecule (by 1.61 kcal mole^{-1} for 7-methylcycloheptatriene) and therefore the tropylium ion is a better hydride ion acceptor (and in general an acceptor of nucleophilic species) than the methyltropylium ion and 7-methylcycloheptatriene is a better hydride ion donor than cycloheptatriene.

Thus Conrow demonstrated, for the methyl group as an example, that a substituent in cations of type (A) has a greater effect on the tropylium ring than on the cycloheptatriene system. The phenyl substituent is known to have an electron-donor effect in some cases[22] and an electron-acceptor effect in others[23]. It has been found that the phenyl group behaves as a weak electron-acceptor substituent in relation to the tropylium ion. The acidity constant pK_S of the phenyltropylium ion[24], measured by Jutz‡, is +3.87. The acidity constant of the tropylium ion in the 1 : 1 acetonitrile–water mixture is $pK_S = 4.01$. Thus the phenyl group destabilises the tropylium ion. Jutz explains this finding by the fact, shown by calculations, that the benzene and tropylium rings are inclined at an angle 45–50°. Such disposition of the rings results in a decrease of the conjugation between the benzene and tropylium systems and the negative inductive effect of the phenyl substituent may be increased thereby.

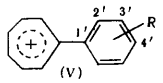
The introduction of seven phenyl substituents destabilises the tropylium ion even more. Due to the very low solubility of heptaphenyltropylium salts, the pK_a value for this ion could not be measured. However, Battiste[25] showed that in a 1 : 1 methanol–acetonitrile mixture methoxycycloheptatriene (III) is fully ionised, with formation of the tropylium ion, under the action of 0.01 N fluoroboric acid, while heptaphenylmethoxycycloheptatriene (IV) is ionised to an extent less than 10% under the action of 1 N acid in the same solution:



‡ Here and henceforth pK_S denotes pK values for carbonium ions measured in a 1 : 1 acetonitrile–water mixture, as was done by Jutz.

Consequently the pK_a value for the heptaphenyltropylium ion is lower by 3 pK units for the tropylium ion, i.e. the heptaphenyltropylium ion is less stable than the tropylium ion in a 1 : 1 methanol–acetonitrile solution by a factor of at least one thousand. It follows from what has been said above that very little is known about the effect of substituents in tropylium ions of type (A) and the quantitative data which have been obtained can be compared only qualitatively.

The effect of substituents bound to the tropylium ring via a benzene ring and a conjugated system of double bonds [cations of type (B)] has been investigated in fair detail. Jutz[24,26] measured the pK_S values for phenyltropylium (V) salts with substituents in the benzene ring.



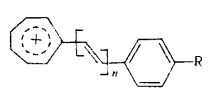
(V)

It was found that these pK_S values are linearly related to Jaffe's σ constants for the substituents [apart from $N(CH_3)_2$], i.e. Hammett's equation holds (see Fig. 1):

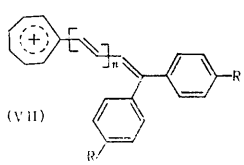
$$pK_s = pK_0 - \sigma\rho;\ \rho = +2.4\ .$$

The positive value of ρ shows that electron-donor substituents reduce the acidity of the phenyltropylium ion, i.e. increase its pK_S value, while electron-acceptor substituents increase its acidity, i.e. lower the pK_S value.

Bearing in mind the disposition of the benzene and tropylium rings at an angle of 45–50°, it may be supposed that in this case the effect of substituents is transmitted as follows: the effect of the substituent R is transmitted by conjugation and inductive mechanisms to position 1′ of the benzene ring in compound (V) and from position 1′ it is further transmitted by an inductive mechanism to the tropylium ring. The introduction of 1, 2, 3, and 4 double bonds between the tropylium and benzene rings in the phenyltropylium ion reduces the acidity of the latter. The pK_S values obtained by Jutz[27,28] for compounds (VI) and (VII) are given below:



(VI)

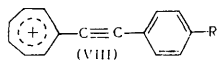


(VII)

for (VI)	R=H	for (VII)	R=H
n	pK_s	n	pK_s
0	3.87	0	4.23
1	4.13	1	4.35
2	4.70	2	4.56

The stabilising effect of conjugated double bonds can be understood if account is taken of their capacity to distribute the positive charge over a large number of centres.

In contrast to the double bond, a triple bond between the tropylium and benzene rings in the phenyltropylium ion greatly increases the acidity of the latter, i.e. decreases the pK_S value: pK_S = +2.40 for the phenylethynyltropylium ion (VIII, R = H)[27], while for the phenyltropylium ion pK_S = +3.87



(VIII)

Consequently the triple bond acts as a powerful electron-acceptor group. It has a similar effect on the ionisation

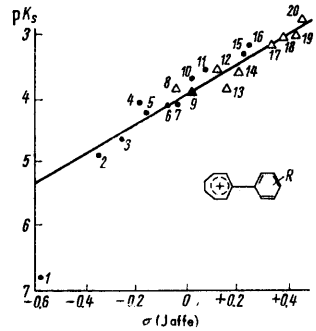
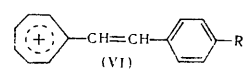


Fig. 1. Variation of the acidity constants pK_S of phenyltropylium cations with Jaffe's σ constants; the substituent R:
1) p-$N(CH_3)_2$; 2) p-OH; 3) p-OCH_3; 4) p-$C(CH_3)_3$; 5) p-CH_3; 6) p-$NHCOC_6H_5$; 7) p-SCH_3; 8) m-CH_3; 9) H; 10) p-C_6H_5; 11) p-F; 12) m-OCH_3; 13) β-naphthyl instead of C_6H_4R; 14) m-C_6H_5; 15) p-Cl; 16) p-Br; 17) m-F; 18) m-Cl; 19) m-Br; 20) m-CF_3.

of acids, for example. Thus phenylpropiolic acid is one hundred times stronger than benzoic acid, while cinnamic acid is somewhat weaker than benzoic acid (see Table 2).

The substituents R in the series of compounds (VI), (VII), and (VIII) have qualitatively the same effect on the stability of the tropylium ion as in the series of compounds (V), namely electron-donor substituents decrease the acidity of the cation, while electron-acceptor substituents increase it. The following pK_S values may be quoted as an example for the styryltropylium series (VI, n = 1):



(VI)

R	H	CH_3	OCH_3	Br	C_6H_5
pK_s	4.13	4.25	4.89	3.82	3.78

However, in contrast to series (V), Hammett's equation does not hold in these cases.

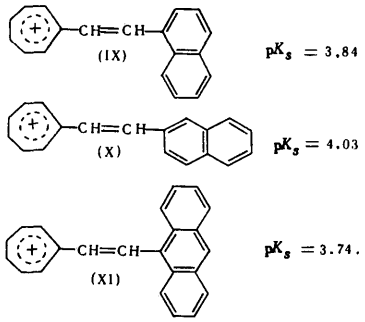
Thus one may conclude that the acidity of tropylium ions of type (B), like that of ions of type (A), increases and decreases respectively in the presence of more powerful electron-acceptor and electron-donor substituents.

The enhanced acidity of (β-arylvinyl)tropylium ions, namely β-(1-naphthyl)- (IX), β-(2-naphthyl)- (X), and β-(9-anthryl), vinyltropylium (XI), ions[29], consitutes an exception. Although these ions have a longer conjugated π-electron system, their acidity is enhanced (the pK_S values are lower) compared with the stability of the styryl-

TABLE 2.

Acid	K_{diss} (in water)
Benzoic	$6 \cdot 10^{-5}$
Cinnamic	$4 \cdot 10^{-5}$
Phenylpropiolic	$6 \cdot 10^{-3}$

tropylium ion (pK_S = 4.13) and even the unsbustituted tropylium ion (pK_S = 4.01):



The acidity of tropylium ions of type (C) changes with the nature of the condensed rings, their number, and position. All six benzotropylium ions known at the present time exhibit greater acidity than the tropylium ion. The pK_a values for benzotropylium ions measured in sulphuric acid are listed in Table 3.

The increase of the acidity (decrease of pK_a) of the tropylium cation condensed with benzene rings is surprising at first sight, since it might have been supposed that in such compounds the positive charge would be more delocalised than in the unsubstituted tropylium ion. However, as already mentioned on p. 735, in the examination of the effect of the substituent on the acidity of the carbonium ion account must be taken of the effect of the substituent both on the cation R^+ and on the pseudobase ROH conjugated with it:

$$R^+ + 2\,H_2O \rightleftarrows ROH + H_3O^+ .$$

Probably the benzene rings condensed with the tropylium ion stabilise the uncharged cycloheptatriene system to a greater extent than the positively charged tropylium ring. This results in a decrease of pK_a. Heilbronner and coworkers[18] calculated the difference between the delocalisation energies of the cation E_{R^+} and the pseudobase E_{ROH}, denoted by A^+_{opt} (the energy of atomic delocalisation), for compounds (XII)–(XVIII):

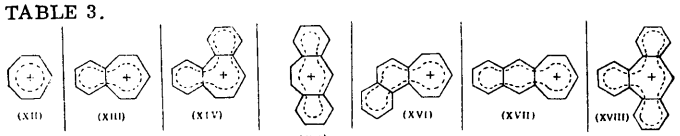
$$A^+_{opt} = E_{R^+} - E_{ROH} .$$

They believe that the entropy and solvation effects and the change in hybridisation are the same for these compounds, i.e. on going from compound (XII) to (XIII), etc. only A^+_{opt} changes. On this basis, it is to be expected that the values of A^+_{opt} are related linearly to the pK_a. The authors showed that such a relation does indeed exist for the cations (XII), (XIII), (XV), (XVI), and (XVII) (see Fig. 2).

The breakdown of coplanarity in the cations (XIV) and (XVIII) leads to a higher acidity of the cation, compared with the values calculated from the plot in Fig. 2.[30]

In contrast to tropylium cations with condensed benzene rings, the tropylium ion condensed with a thiophen ring (XIX) is much more stable than the unsubstituted tropylium

TABLE 3.



+4.7[2] | +1.7±0.1[15] | −2.9±0.3[16] | −1.9±0.1[17] | +2.2±0.1[18] | +0.3±0.1[16] | −7.4[19]

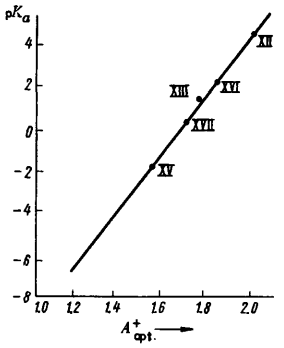
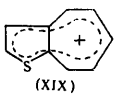


Fig. 2. Variation of the pK_a values for benzotropylium ions with the atomic delocalisation energy A^+_{opt}.

ion[31]: the pK_a value for this cation is +6.05 (pK_a = +4.75 for the tropylium ion).



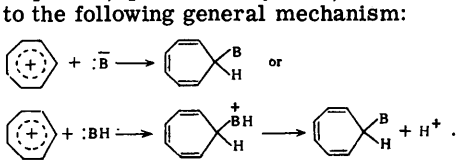
(XIX)

Thus the introduction of the substituent linked to the tropylium ring by a single σ-bond [ions of types (A) and (B)] alters the acidity of the cation in a manner depending on the electron-donor or electron-acceptor properties of the substituent. Electron-donor substituents reduce the acidity of the tropylium ion and electron-acceptor substituents increase it. The explanation of this is probably that such substituents have a much greater effect on the positively charged seven-membered tropylium ring than on the uncharged cycloheptatriene system. On the other hand, in cations of type (C), for example the benzotropylium ion, the condensed benzene rings stabilise the cycloheptatriene system to a greater extent than the tropylium system, and this has been confirmed by calculations. This leads to an increase of the acidity of the benzotropylium ions, i.e. a decrease of their pK_a values, compared with the unsubstituted tropylium ion.

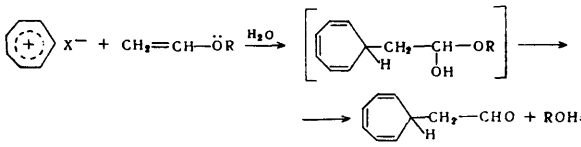
III. REACTIONS WITH TRANSFER OF ELECTRONS TO THE TROPYLIUM ION

1. The Tropylium Ion as the Acceptor in Charge-Transfer Complexes

As already mentioned, the tropylium cation is one of the most stable carbonium ions and it therefore constitutes an excellent model for the investigation of the properties of carbonium ions. The positive charge of the tropylium ion is responsible for its intense electron-acceptor properties, as in other carbonium ions. Thus the tropylium ion readily reacts with nucleophilic agents, for example with complex alkali metal hydrides[32], alkoxides, organometallic compounds, potassium cyanide, ammonia[2,9], etc. according to the following general mechanism:



The tropylium ion reacts readily also with compounds containing a double bond activated by electron-donor substituents, for example with vinyl ethers[33]:



The electron-acceptor properties of the tropylium ion are not shown only in their capacity to add to reaction centres at which there is an enhanced electron density, with formation of a covalent bond. In some cases the tropylium ion can form charge-transfer complexes, playing the role of the acceptor.

Usually the formation of a charge-transfer complex is detected from the appearance in the absorption spectra of new bands which are not characteristic either of the donor or the acceptor separately in the same solvent; this is accompanied by a deepening of the colour. McConnel[34] showed that the charge-transfer energy $E_{ct} = h\nu$ is linearly related to the ionisation potential of the donor and the electron affinity of the acceptor. The ionisation potentials or the electron affinities can be measured, for example by polarography; if there is a linear relation between the observed wavelengths of the maxima in the absorption spectra and the ionisation potentials, the formation of charge-transfer complexes is demonstrated. Such a linear relation has been obtained experimentally in a number of cases[35].

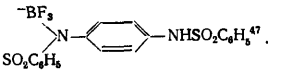
Charge-transfer complexes with the tropylium ion as the acceptor were observed for the first time by Feldman and Winstein[36]. They found that, when aromatic hydrocarbons are added to solutions of tropylium perchlorate and fluoroborate in dichloroethane and acetonitrile, new absorption bands, which are not characteristic either of the hydrocarbons or of the tropylium ion, appear in the ultraviolet and visible spectra (Table 4).

The observed wavelengths of the absorption bands are linearly related to the wavelengths of the absorption maxima of the charge-transfer complexes formed by the same donors with other acceptors, for example trinitrobenzene, iodine, or tetracyanoethylene. The energies of charge transfer from benzene, naphthalene, and anthracene to the tropylium ion have been calculated by the molecular orbital method as $E = h\nu = 1.445\beta$, 1.063β, and 0.859β respectively[1], whence λ_{max} = 322, 438, and 540 nm. The calculated data are in good agreement with those found experimentally (Table 4). On the basis of these results, the authors attributed the new absorption bands to charge transfer complexes of the tropylium ion and the aromatic hydrocarbons.

The tropylium ion forms charge-transfer complexes also with other donors, for example with certain anions.

As already stated above, the tropylium ion combines with certain nucleophilic species, in particular anions, with formation of a covalent bond. Highly nucleophilic ions give rise to a covalent bond, while weakly nucleophilic anions form ionic bonds with the tropylium ion. Vol'pin et al.[37] showed that the transitions from ionic tropylium compounds $C_7H_7^+X^-$ to covalent cycloheptatriene derivatives C_7H_7X occurs in the range of the K_a values of the corresponding acids between 1.2×10^{-4} (HNCO) and $(6.3-7.75) \times 10^{-5}$ (C_6H_5COOH and CH_3COOH), i.e. acids with $K_a > 1.2 \times 10^{-4}$ form ionic compounds with the tropylium ion, while those with $K_a < 6.3 \times 10^{-5}$ form covalent compounds.

A large number of ionic tropylium compounds are known at the present time, namely salts with the following anions: Br^-, Cl^-, I^-, BF_4^-,[38] SiF_6^-, ClO_4^-, $PtCl_6^{2-}$, $B(C_6H_5)_4^-$, HgI_4^{2-}, $HgBr_4^{2-}$,[3] BCl_4^-, BBr_4^-, BI_4^-,[39-43] HCl_2^-, HBr_2^-,[44] $SnCl_6^{2-}$,[45] $SnBr_6^{2-}$, $AlCl_4^-$, $FeCl_4^-$,[46]



Their ultraviolet spectra, polarographic behaviour, and magnetic properties as well as X-ray diffraction studies show[3] that all these compounds contain the same cation $C_7H_7^+$. Thus there is now no doubt about the capacity of the tropylium ion to form ionic bonds with certain anions. However, some anions are capable of forming charge-transfer complexes with the tropylium cation under certain conditions.

Doering[8] explained the colour of tropylium halides by the formation of charge-transfer complexes. Kitaigorodskii et al.[4] pointed out the possible presence of a weak charge-transfer bond between the seven-membered ring and the iodide anion in crystalline tropylium iodide. Harmon and coworkers showed[48,49] that the absorption spectra of tropylium halides in methylene chloride (a solvent with a low dissociation capacity and a dielectric constant ϵ = 9.08) contain new bands, compared with the spectra of tropylium halides in sulphuric acid, for example (Table 5).

In contrast to the halides, the solutions of tropylium perchlorate and fluoroborate are not coloured and do not show absorption bands in the long-wavelength region. The halide solutions retain their colour only when fresh and therefore the colour is not due to decomposition products or polarisation, as sometimes happens. The wavelengths of the maxima in the absorption spectra are linearly related to the ionisation potentials of the anions.

On the basis of the results obtained, Harmon et al.[48,49] concluded that in solution in methylene chloride the tropylium ion forms charge-transfer complexes (CTC) with halide anions. Such complexes are not formed with the anions BF_4^- and ClO_4^-. In more polar solvents the absorption bands due to charge transfer disappear. This is consistent with the properties of other charge-transfer complexes, the positions of the absorption maxima of which depend on the polarity of the solvent. Kosower showed

TABLE 4.

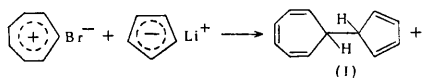
Hydrocarbon	λ_{max} in $ClCH_2CH_2Cl$, nm	λ_{max} in CH_3CN, nm	Hydrocarbon	λ_{max} in $ClCH_2CH_2Cl$, nm	λ_{max} in CH_3CN, nm
Benzene	305	—	Naphthalene	430	395
Toluene	325	310	2-Methylnaphthalene	472	—
m-Xylene	—	330	Phenanthrene	425	—
p-Xylene	340	323	Anthracene	530	487
Mesitylene	365	350	Pyrene	535	—

TABLE 5.

Salt	$C_7H_7^+Cl^-$	$C_7H_7^+Br^-$	$C_7H_7^+I^-$
λ_{max} (additional) in CH_2Cl_2, nm	293	402	422

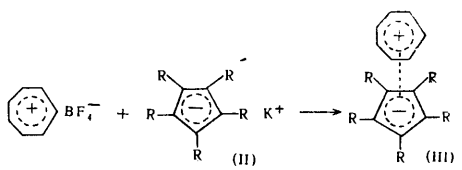
that the dependence of the position of the maxima in the absorption spectra of charge-transfer complexes on the nature of the solvent is represented by a straight line when a special quantity Z characterising the polarity is introduced[50]. It was found that the energy of charge transfer for tropylium iodide in various solvents is also linearly related to Z (Fig. 3)[51].

Thus halide anions occupy a middle position among other anions as regards their nucleophilic properties: they form ionic compounds with the tropylium ion but they are sufficiently nucleophilic to give rise also to a charge-transfer complex. It is reasonable to expect that certain organic anions forming a covalent bond with the tropylium ion may form charge-transfer complexes with the tropylium ion when electron-acceptor substituents are introduced into the anions. In fact, on interaction with the tropylium ion, lithium cyclopentadienide forms a covalent compound—(1-cyclopentadienyl)cycloheptatriene[37]:



(I)

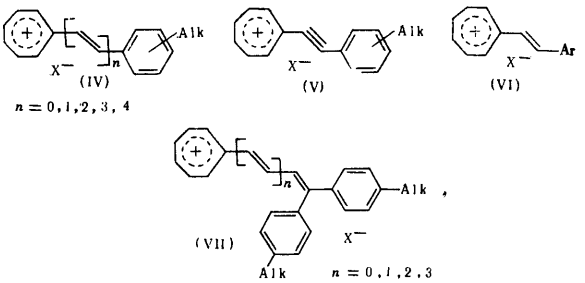
In contrast, LeGoff and La Caunt[52] showed that with potassium 1,2,3,4,5-pentamethoxycarbonylcyclopentadienide the tropylium ion forms a salt-like compound (III), with an absorption maximum in the region of 470 nm, which is not characteristic of the individual ions, i.e. a charge-transfer complex forms:



(II) (III)

where R = $COOCH_3$.

In the cases described the tropylium ion is the acceptor, while the donors are either hydrocarbon molecules or anions. However, Jutz showed that substituted tropylium cations (IV)–(VII), with substituents having a mobile π-electron system, also exhibit certain properties characteristic of charge-transfer complexes[24,27-29]. Jutz calls these cations "internal" charge-transfer complexes, in which the tropylium ring is the acceptor and the substituent is the donor:



(IV) (V) (VI)

$n = 0, 1, 2, 3, 4$

(VII)

$n = 0, 1, 2, 3$

where Ar = phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthryl, 3-pyrenyl, and 9-anthryl and X = ClO_4 and BF_4. In fact all these salts are coloured (they absorb in the long-wavelength region of the spectrum). All the cations (IV)–(VII) are characterised by negative solvatochromism (displacement of the absorption maxima into the long-wavelength region on going to less polar solvents), which is shown mainly in the long-wavelength absorption maxima. Electron-donor substituents have a powerful effect on the positions of these absorption maxima, displacing them towards longer wavelengths. Furthermore, Jutz showed that for the cations (VI) there is a linear relation between the energies $E = h\nu$ (for the long-wavelength maxima) and the ionisation potentials $E_{1/2}$ of methyl-substituted hydrocarbons corresponding to the substituents[24,27-29,53]. Consequently interaction of the donor–acceptor type takes place in charge-transfer complexes between the tropylium ring and the substituents in the cations (IV)–(VI).

Thus the tropylium ion can form ionic and covalent bonds and also donor–acceptor bonds in charge-transfer complexes. The latter are of great theoretical interest, since they are logical intermediates in reactions involving nucleophilic addition to carbonium ions, both stable and transient, which are formed in many reactions.

2. Electron Transfers to the Tropylium Ion

In the discussion of charge-transfer complexes as intermediates in reactions it is assumed that the first stage of the reaction is displacement of electron density, while the interchange of nuclei and their fixation in new positions constitute a secondary process[54]. However, one could imagine that in some cases the displacement of electron density may be followed by electron transfer without displacement of the nucleus. In the case of the tropylium ion the tropyl radical C_7H_7 or its dimerisation product (ditropyl) should then form. The possibility of such chemical reactions with the tropylium ion is confirmed by the high conjugation energy of the tropyl radical, which, according to Streitwieser's calculations[55], is -2.54β, and also by the low potential of the one-electron electrochemical reduction of the tropylium ion, which is 1.2 V§.[56]

In fact, Doering[9] showed that ditropyl forms in the interaction between a tropylium salt and zinc dust in aqueous solution. According to Vol'pin's data[58], the

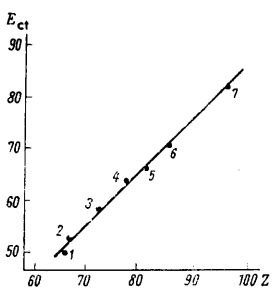
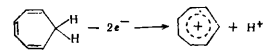


Fig. 3. Variation of the charge transfer energy E_{ct} of tropylium iodide in various solvents with the quantity Z characterising the polarity of the solvent:
1) methylene chloride; 2) acetone; 3) acetonitrile; 4) isopropyl alcohol; 5) ethyl alcohol; 6) methyl alcohol; 7) water.

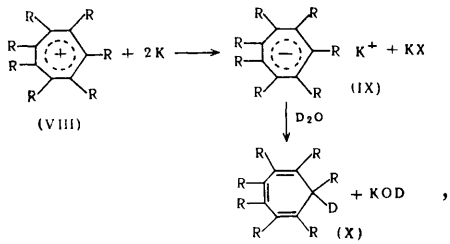
§ It is interesting to note that the tropylium ion forms in the electrochemical oxidation of cycloheptatriene, i.e. two-electron oxidation takes place[57]:



tropylium ion reacts similarly with other metals, even noble metals, i.e. tropyl behaves as a metal located on the right-hand side in the potential series. Probably tropyl radicals are formed in the reaction, and their dimerisation leads to the formation of ditropyl:

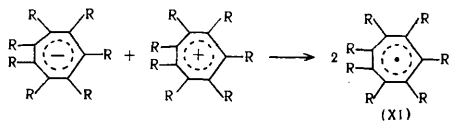


Indeed, under special conditions, namely when freshly sublimed tropylium bromide reacts with a sodium–potassium alloy in dimethoxyethane solution at −80°C, dos Santos-Veiga[59] succeeded in measuring the ESR spectrum of the tropyl radical. In some cases there is a possibility of the transfer of two electrons to the tropylium ring with the formation of a seven-membered anion. Thus Breslow and Chang[60,61] showed that the reaction of the heptaphenyltropylium ion (VIII) with metallic potassium leads to the formation of potassium heptaphenylcycloheptatrienide (IX), which is soluble in dimethoxyethane but insoluble in ethyl ether. In the reaction with D_2O there forms potassium hydroxide and deuterioheptaphenylcycloheptatriene (X), whose structure has been demonstrated by NMR spectroscopy:



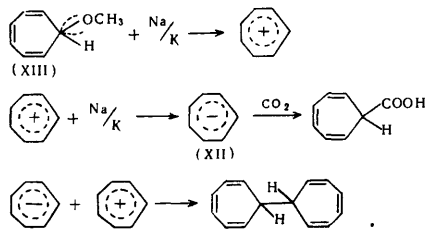
where R = C_6H_5.

When the anion (IX) reacts with an excess of a tropylium salt, there forms a radical (XI), which gives rise to an ESR signal (the anion does not exhibit paramagnetic properties):



where R = C_6H_5.

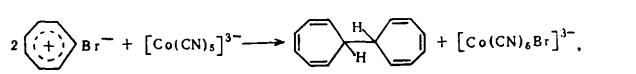
Dauben explained by a two-electron transfer the formation of the unsubstituted cycloheptatrienide anion (XII).[62] He showed that, when methoxycycloheptatriene (XIII) is added slowly to a solution of the sodium–potassium alloy in tetrahydrofuran at −20°C, a blue solution forms, whose subsequent carboxylation yields ditropyl and cycloheptatriene-7-carboxylic acid, which is evidence of the formation of the anion as an intermediate. Dauben suggests the following reaction mechanism:



The C–O bond in methoxycycloheptatriene undergoes ionic dissociation with formation of the tropylium ion, which is further reduced by the alkali metal to the anion, yielding on carboxylation cycloheptatrienecarboxylic acid¶. One-electron transfer from the anion to the tropylium ion yields ditropyl.

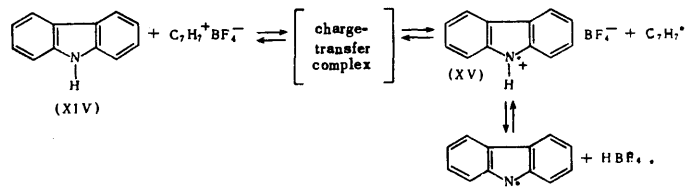
It is noteworthy that Bauld and Brown[63] succeeded in demonstrating with the aid of ESR spectroscopy that during this reaction there is a possibility of the transfer of yet another electron to the cycloheptatrienide anion with the formation of a radical-dianion.

The tropylium ion may be reduced to ditropyl by transition metal complexes, for example[64]:

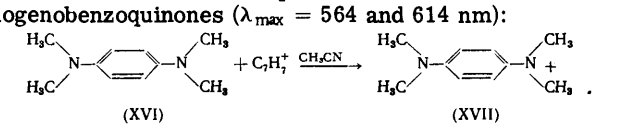


$NaMn(CO)_5$, $KFe(CO)_nH$, $HgFe(CO)_n$,[65] $V(CO)_6$, and $Na[C_5H_5Cr(CO)_3]$[66] have a similar effect on the tropylium ion.

Ledwith and coworkers[67,68] showed that the tropylium ion can remove electrons from certain heterocyclic compounds containing a double bond or an aromatic ring. The latter form radical cations on giving up an electron. Thus carbazole (XIV) is oxidised by the tropylium ion to the radical-cation (XV), whose structure has been demonstrated by NMR, infrared, and ESR ($g \simeq 2$) spectroscopy.

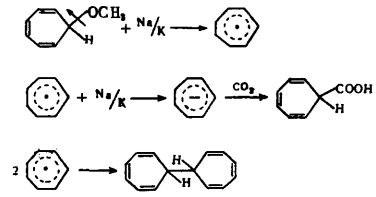


The radical-cation (XV) contains a labile hydrogen atom, as a result of which it is unstable. When *N*-methylcarbazole was used, a radical-cation stable in neutral solution was obtained. To confirm the occurrence of one-electron transfer to the tropylium ion, *NN*-tetramethyl-*p*-phenylenediamine (XVI), which is known to form radical-cations with other acceptors, for example halogenobenzoquinones[69], was used as the reducing agent. It was found that in the reaction with the tropylium ion it forms a radical-cation (XVII) which is identical with that produced in the reaction with halogenobenzoquinones (λ_{max} = 564 and 614 nm):



Unfortunately, in none of their experiments did the authors isolate ditropyl, whose formation would constitute important evidence of the occurrence of one-electron transfer to the tropylium ion.

¶ Although heterolytic dissociation of the C–O bond in cycloheptatriene derivatives under the action of electrophilic agents is widely known in the chemistry of the tropylium ion, we believe that in this case one cannot entirely exclude the possibility of homolytic dissociation:



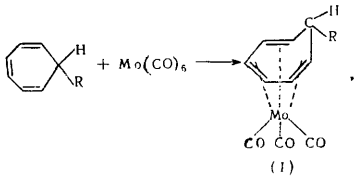
Thus the electron-acceptor properties of the tropylium ion, which is a carbonium ion, are shown not only in its capacity to combine with a species having an electron pair, but also in its capacity to combine with electrons. One-electron transfer to the tropylium ion leads to the formation of the tropyl radical or its dimer and two-electron transfer leads to the formation of the cycloheptatrienide anion. Systems with less mobile electrons can form charge-transfer complexes with the tropylium ion.

IV. SANDWICH COMPOUNDS OF THE TROPYLIUM ION

Sandwich compounds of transition metals with cyclopentatrienyl and arene ligands are widely known at the present time. Many studies have been made on their synthesis and properties. The sandwich compounds of transition metals in which the ligands are C_7H_7 rings have been almost not investigated.

Like the cyclopentadienyl and benzyl rings, the cycloheptatrienyl ring has six π-electrons which can form a bond with a central metal atom. Physical measurements, namely X-ray diffraction analysis and NMR and infrared spectra, have shown that, as a rule, all the carbon atoms of the cycloheptatrienyl ring are identical and lie in one plane. On this basis, one can postulate that the seven-membered ring in such complexes has the structure of the tropylium ion and the complexes may be regarded as tropylium complexes of transition metals.

Attempts to obtain transition metal complexes with the tropylium cation were made soon after its synthesis by Doering[2]. Wilkinson[65,70] was the first to attempt the preparation of a tropylium complex of this kind. In the reaction of a metal carbonyl with cyclopentadiene or benzene three carbonyl groups are capable of being replaced by the cyclopentadienide or benzene system, hydrogen being removed from cyclopentadiene in the reaction with the latter. Wilkinson hoped that in the reaction between cycloheptatriene and molybdenum hexacarbonyl the carbonyl group would also be replaced by the tropylium aromatic system with simultaneous removal of the hydrogen atom. However, the latter did not occur and Wilkinson obtained cycloheptatrienemolybdenum tricarbonyl (I). The reaction with cycloheptatriene derivatives took place similarly:

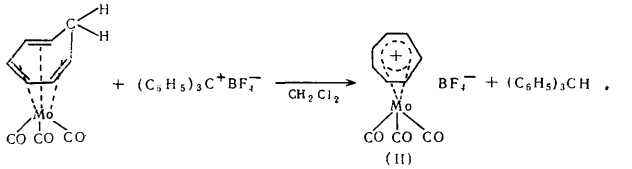


(I)

where R = H, C_6H_5, C_7H_7, OC_7H_7.

The attempts to prepare the desired complex by introducing tropylium bromide directly into the reaction were also unsuccessful.

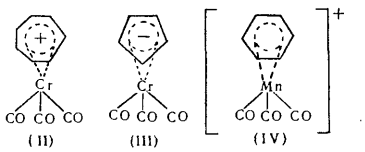
Dauben succeeded in preparing a tropylium complex[71]. Before this he established that, when salts of the triphenylmethyl cation are allowed to act on cycloheptatriene and its derivatives, a hydride ion migrates from cycloheptatriene to the carbonium ion with formation of a tropylium salt and triphenylmethane[38]. An analogous reaction with the cycloheptatrienemolybdenum tricarbonyl obtained by Wilkinson would yield tropylium-molybdenum tricarbonyl (II). The reaction did indeed take place, and the required complex (II) was obtained in quantitative yield:



(II)

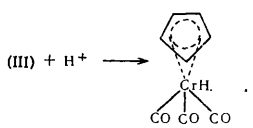
Compound (II) is more symmetrical than the cycloheptatriene complex (I). The greater symmetry of compound (II) is shown in the fact that the infrared spectra have only two carbonyl maxima, analogous to the absorption maxima of cyclopentadienylmanganese tricarbonyl and benzenechromium tricarbonyl, while three carbonyl maxima are observed in the spectrum of the cycloheptatriene complex. NMR spectra reveal the presence of protons of only one type, which confirms the highly symmetrical structure of the complex, with the metal atom bound to all seven carbon atoms of the seven-membered ligand. Complexes with chromium and tungsten were obtained similarly[72,73].

Pauson compared the sandwich cations obtained by Dauben with charged complexes of the type of cyclopentadienylchromium tricarbonyl (III) and benzenemanganese tricarbonyl (IV):[74]

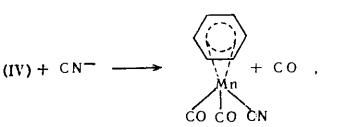


(II) (III) (IV)

Pauson believes that the negative charge in complex (III) is mainly localised in the ring although it is reduced by the action of the electron-acceptor group $M(CO)_3$. However, the addition of a positively charged species to the ring† would lead to the breakdown of the inert-gas electron shell of the system as a whole. Therefore the addition of an electrophilic agent, for example a proton, to the metal atom with formation of a carbonyl hydride is energetically more favourable:

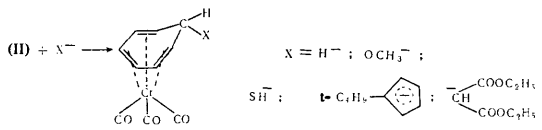


As a result of the same factors as those postulated for compound (III), the positive charge in complex (IV) is distributed between the benzene ring and the metal and again there is no addition of a nucleophilic species to the ring. However, in contrast to compound (III), a nucleophilic species does not add to the metal atom either, since manganese does not have vacant orbitals and therefore reaction, with a cyanide ion for example, can take place only with displacement of a carbonyl group:



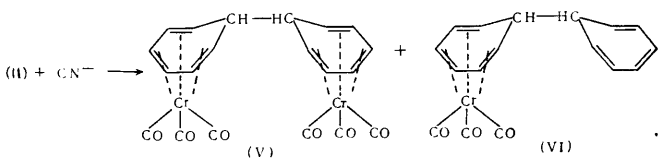
† In this and other cases where a species adds to a ligand or a metal atom only the final products are considered and not the reaction mechanism.

Pauson believes that, in contrast to these compounds, the tropylium complex (II) has a positive charge on the ring, the charge being enhanced further by the electron-acceptor effect of the $M(CO)_3$ group. The addition of nucleophilic species to the ring can result in this case in stable final products, due to the formation of a cycloheptatriene ring linked to the metal atom via six π-electrons, i.e. the inert-gas shell does not break down. In fact the cation (II) does react with certain nucleophilic agents, cycloheptatriene complexes being formed[75]:



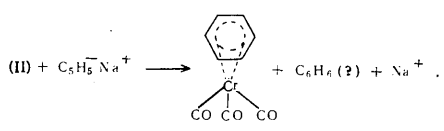
This reaction is analogous to the reactions of the free tropylium ion. Pauson called it the "normal" reaction of tropyliumchromium tricarbonyl salts with anions.

Apart from the "normal" reaction characteristic of the free tropylium ion, reactions characteristic of the system as a whole, with some similarities to those of other carbonyl complexes, were to be expected for complex (II). Pauson and Munro hoped to replace the carbonyl group by a cyanide ion, as happens in benzenemanganese tricarbonyl, already mentioned, and other complexes. However, the reaction of tropyliumchromium tricarbonyl with sodium cyanide takes place in a different manner. Apart from a small amount of the product of the "normal" addition, the authors isolated substances with structures (V) and (VI):[76]

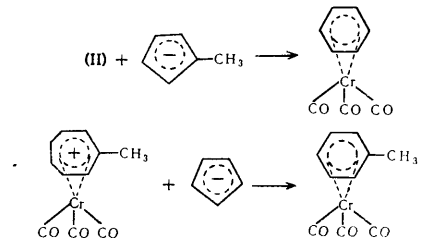


The reaction with $NaHCO_3$, CH_3COONa, $NaNH_2$, C_6H_5Li, $C_6H_5\overset{O}{\overset{\|}{C}}NH_2$, and HCl (2 *N*) takes place similarly. This process was called the "anomalous" reaction of complex (II) with anions.

Attempting nevertheless to replace the carbonyl groups in tropylium chromium tricarbonyl by a nucleophilic species, Pauson and Munro allowed the cyclopentadienide anion, which has a considerable affinity for the metal, to react with the complex. To their surprise, they failed to isolate after the reaction the products of either the "normal" or the "anomalous" addition. Instead they obtained benzenechromium tricarbonyl[73,77]:

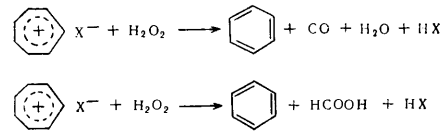


Benzenechromium tricarbonyl is also obtained in the reaction between tropyliumchromium tricarbonyl and sodium methylcyclopentadienide. On the other hand, the reaction between methyltropyliumchromium tricarbonyl and sodium cyclopentadienide results in the formation of toluenechromium tricarbonyl:



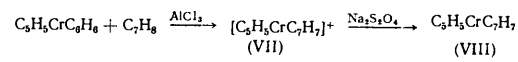
Thus benzene bound to chromium is obtained as a result of the contraction of the seven-membered ring of complex (II). To confirm this finding completely, the authors used in the reaction a tropylium complex labelled with tritium and indeed they observed the expected activity in the benzenechromium tricarbonyl. The contraction of the tropylium ring to the benzene ring in compound (II) was also found to occur in the reaction with sodiomalonic ester in the presence of an excess of the complex (in the presence of an excess of the sodiomalonic ester the reaction takes place with formation of "normal" addition products). Hence the authors concluded that the "normal" product forms first and then ring contraction takes place.

The rearrangement of the seven-membered ring to a six-membered ring with simultaneous elimination of one carbon atom is also known in the chemistry of free tropylium ions. Vol'pin et al. showed[78] that, when a dilute aqueous solution of hydrogen peroxide is allowed to act on the tropylium ion at room temperature, benzene in 80% yield, carbon monoxide, and formic acid are formed:

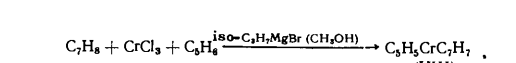


The "anomalous" addition reaction and the reactions involving the contraction of the seven-membered ring showed that the tropylium complexes obtained for the first time by Dauben are new systems, whose study is of great interest.

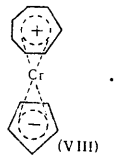
Apart from these complex cations, uncharged sandwich compounds of the tropylium ion have been described. If the three carbonyl groups in cycloheptatrienylchromium tricarbonyl are replaced by the cyclopentadienyl residue, the molecule will be uncharged as a whole. Such a complex (VIII) was obtained by Fischer from cyclopentadienylbenzenechromium and cycloheptatriene in the presence of aluminium chloride, with subsequent hydrolysis of the reaction mixture and the reduction with sodium hydrosulphite of the cation (VII) formed initially[79]:



Somewhat later King and Bisnette[80] obtained the same complex (VIII) by a more convenient method, involving the reaction of isopropylmagnesium bromide with a mixture of chromium trichloride, cyclopentadiene, and cycloheptatriene in ethereal solution at −78°C with subsequent alcoholysis of the reaction mixture:

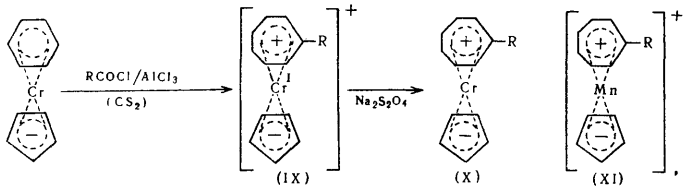


The NMR spectra of compound (VIII) revealed the presence of two types of protons in a ratio of 5 : 7. The infrared spectra also correspond to conjugated five- and seven-membered rings. The dipole moment is 0.79 D in benzene. On the basis of these data, and also in view of the tendency of the C_7H_7 and C_5H_5 systems to undergo conversion into the ions $C_7H_7^+$ and $C_5H_5^-$, a structure with partial positive and negative charges on the seven-membered and five-membered rings respectively may be put forward for compound (VIII):



(VIII)

Similar complexes with an unsubstituted tropylium ring were unexpectedly obtained by Fischer (in 10% yield) in attempts to acylate cyclopentadienylbenzenechromium by the Friedel–Crafts method[81]:



(IX) (X) (XI)

where R = CH_3 or C_6H_5. The cation (IX) formed initially yields on reduction the uncharged complex (X), which has an inert-gas electron shell. With manganese, which has in its shell one electron more than chromium, the tropylium cation (XI), with 18 π-electrons, forms immediately.

Both complexes have similar infrared spectra and the NMR spectra reveal three types of protons in ratios of 6 : 5 : 3 (for R = CH_3), which is consistent with structures (X) and (XI). To confirm the tropylium structure of the ligand, the authors, using Dauben's method, obtained from the cycloheptatriene complex a compound identical with compound (X).

The paramagnetic cycloheptatrienylcyclopentadienylvanadium, obtained by King and Stone[82] in the reaction between cycloheptatriene and cycloheptadienylvanadium tetracarbonyl:

$$C_5H_5V(CO)_4 + C_7H_8 \rightarrow C_5H_5VC_7H_7 ,$$

and also the diamagnetic cycloheptatrienylvanadium tricarbonyl[65] have structures similar to that of complex (X). The planarity of the seven-membered ring and its high symmetry have been demonstrated by X-ray diffraction measurements[83] and also by NMR and infrared spectroscopy[65,84].

The platinum complex (XII), obtained by Fischer and Fritz[85], is somewhat exceptional. The infrared spectra of this complex are very similar to those of tropylium bromide and differ markedly from the spectra of cycloheptatriene. On the basis of these data, the authors assert that the seven-membered ligand has the tropylium structure:

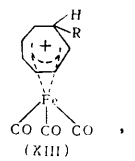
$$PtBr_4 + C_7H_8 \rightarrow (C_7H_7PtBr_2)_2 .$$

(XII)

Thus at the present time only synthetic methods and certain physical properties, which suggest a tropylium structure of the seven-membered ring, have been described for uncharged complexes with the seven-membered ligand.

So far tropylium complexes of transition metals in which an inert-gas electron shell was achieved (the paramagnetic cycloheptatrienylcyclopentadienylvanadium, which has one unpaired electron, is an exception) were considered. Metals of Group VIB then remain zerovalent, vanadium in tropylium vanadium tricarbonyl[65] has a valence of –1, and the cyclopentadienyltropylium-manganese complex[81] is a cation. Analogous complexes of iron, i.e. complexes with a tropylium ligand, for example $[C_7H_7Fe(CO)_3]^+$, would have two electrons more than the corresponding inert gas, or, if Sidgwick's rule holds, would be triply charged cations. Attempts have been made to synthesise such complexes and to determine their structure.

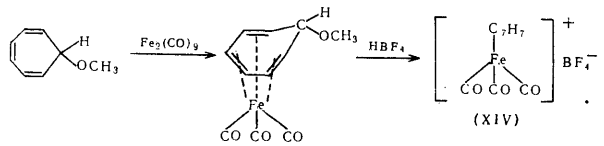
Dauben[72] tried to prepare a complex of iron and the C_7H_7 ligand in the reaction between the triphenylmethyl cation and cycloheptatrieneiron tricarbonyl. However, instead of the removal of a hydride ion, the carbonium ion added to the double bond of the cycloheptatriene ring with formation of the cation (XIII):



(XIII)

where R = $(C_6H_5)_3C$.

It appears that Pettit and coworkers[86] succeeded in obtaining the desired complex $[C_7H_7Fe(CO)_3]^+BF_4^-$ (XIV) by the action of methoxycycloheptatriene on iron carbonyl with subsequent decomposition with acid of the methoxycycloheptatrieneiron tricarbonyl produced:



(XIV)

However, the study of the chemical properties of compound (XIV) suggests that the ligand C_7H_7 is more likely to have the tropylium structure. Indeed hydrolysis of complex (XIV) yields a complex of tropyl alcohol $C_7H_7OHFe(CO)_3$. Acid decomposition of the latter again results in the formation of compound (XIV). A similar reaction also occurs in the chemistry of the free tropylium ion:

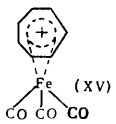
$$C_7H_7^+ + H_2O \rightleftarrows C_7H_7OH + H^+ .$$

Only one signal is observed in the NMR spectra of complex (XIV), i.e. there is only one type of proton. This confirms the symmetrical tropylium structure of the ligand C_7H_7. However, the authors observed in the infrared spectra three absorption bands in the region of C–H vibrations instead of one, as would be expected for the symmetrical C_7H_7 ligand. Comparison of the acidity constants of complex (XIV) and the free tropylium ion (Table 6) shows that the cation (XIV) is less stable than the tropylium cation, while the tropylium complexes of Group VIB metals are more stable than the tropylium cation itself.

TABLE 6.

	pK_a in water		pK_a in water
(1) C_7H_7	+4.7	(4) $C_7H_7W(CO)_3$	+6
(2) $C_7H_7Cr(CO)_3$	+6.3	(5) $C_7H_7Fe(CO)_3$	+4.5
(3) $C_7H_7Mo(CO)_3$	+6.2	(6) $C_7H_9Fe(CO_3)$	+4.7

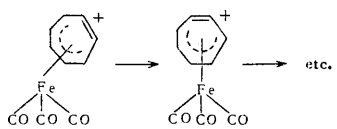
Therefore the structure of the tropylium complex (XIV) cannot be that of compound (XV):



(XV)

It follows from Table 6 that the pK_a values for the cations of cycloheptatrienyliron tricarbonyl (5) and cycloheptadienyliron tricarbonyl (6) are approximately equal. The study of the infrared spectra of the cation (XIV) showed that the vibrations of the carbonyl groups in this complex occur in the same region as the vibrations of the carbonyl groups in dienyliron tricarbonyl complexes (2070 cm^{-1} and 2120 cm^{-1}). Furthermore, the presence of an absorption band in the region of 731 cm^{-1} enabled the authors to suggest the presence of a *cis*-double bond.

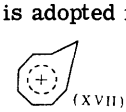
On the basis of these results, Pettit and coworkers concluded that the cation (XIV) has the structure (XVI), analogous to that of cationic cyclopentadienyliron tricarbonyl, the inert-gas electron shell being achieved in complex (XVI):



(XVIa) (XVIb)

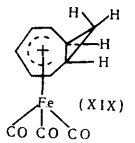
The identity of the protons revealed in the NMR spectra is explained by the rotation of the $Fe(CO)_3$ group about the seven-membered ring, which leads to the tautomers (XVIa), (XVIb), etc.

In conclusion we shall consider transition metal complexes with protonated cyclo-octatetraene as the ligand. Rosenberg et al.[87] showed that the NMR spectrum of free protonated cyclo-octatetraene $C_8H_9^+$ has four peaks with relative areas of 5 : 2 : 1 : 1. On this basis, the authors suggested that seven carbon atoms lie in one plane, forming a tropylium ring (this accounts for the stability of the cation), while the methylene group lies outside this plane. Thus the structure (XVII) is adopted for the cation $C_8H_9^+$.


(XVII)

Winstein and coworkers[88] found that the NMR spectra of the complex cation $[C_8H_9Mo(CO)_3]^+$ also reveal the presence of four types of proton in the ratios 5 : 2 : 1 : 1. Consequently the structure of the cation $C_8H_9^+$ [structure (XVII)] persists also in the complex (XVIII), which leads to the participation of six π-electrons in the formation of a metal–ligand bond and a stable common 18 π-electron shell. Thus the structure of protonated cyclo-octatetraenemolybdenum tricarbonyl (XVIII) resembles closely that of tropyliummolybdenum tricarbonyl.

Different workers have attributed different structures to the analogous iron complex[89,90]. Very recently Winstein and coworkers[88] showed, on the basis of a thorough study of the NMR spectra of protonated cyclo-octatetraeneiron tricarbonyl, that this complex has the structure (XIX), similar to the structure of dienylirion tricarbonyl, as for the complex $[C_7H_7Fe(CO)_3]^+$ [complex (XVI)]:



(XIX)

Complexes with the ligand C_7H_7 are now known for metals of Groups VB, VIB, VIIB, and VIII, examples being vanadium (Group V), chromium and molybdenum (Group VI), manganese (Group VII), and iron and platinum (Group VIII). In all these complexes, except for the iron complex, the seven-membered ligand has the tropylium structure and almost all the complexes obey Sidgwick's rule. Exceptions are the paramagnetic cycloheptatrienylcyclopentadienylvanadium $C_7H_7VC_5H_5$, the electron shell of which consists of 17 π-electrons, and the platinum complex $(C_7H_7PtBr_2)_2$, which probably has a shell consisting of 20 π-electrons. In the iron complex (XVI) four π-electrons form a metal–ligand bond of the type which exists in diene complexes and a shell of 18 π-electrons is formed.

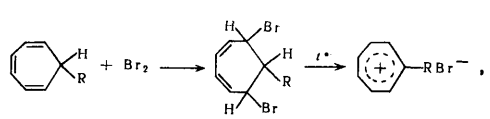
There are virtually no data at the moment concerning the reactivity of these complexes. Only certain reactions of the tropyliumchromium tricarbonyl cation are known[75-77]. The chemical properties of the uncharged complexes have not been investigated at all. It is not possible as yet to predict their behaviour in reactions, since the distribution of electron density, which is primarily responsible for chemical reactions, cannot be measured by methods available at the present time, and calculations yield very ambiguous answers (as shown by the calculation for the ferrocene molecule).[91,92] Nevertheless, there is no doubt that further studies will lead to interesting and unexpected reactions of these complexes, a feature which is characteristic of the chemistry of the sandwich compounds of transition metals in general.

V. FORMATION OF THE TROPYLIUM ION AND ITS PROPERTIES

1. Formation of the Salts of Substituted and Unsubstituted Tropylium Ions

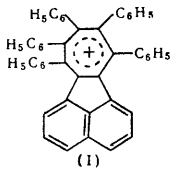
One of the characteristic properties of aromatic systems is known to be the ease of their formation. This applies also to the tropylium cation. The ways in which substituted and unsubstituted tropylium ions are formed are presented below.

1. Doering's method[2] consists in the bromination of cycloheptatriene and its derivatives with subsequent dehydrobromination under conditions of mild pyrolysis:



where R = H, COOH, C_6H_5, t-C_4H_9, and Br. Salts of carboxytropylium[20,93,94], phenyl-, t-butyl-, and bromotropylium[8], and also heptaphenyltropylium[25], and

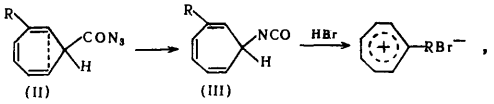
7,8,9,10,11-pentaphenylcyclohepta-acenaphthenylium[95] ions (I):



(I)

were obtained by this method.

2. The method of Dewar and Pettit[96,97] consists in heating the azides of norcaradienecarboxylic acid (II) in benzene with subsequent treatment of the resulting isocyanate (III) with hydrogen bromide:

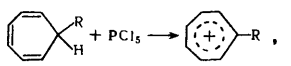


(II) (III)

where R = H and CH_3.

3. The removal of a hydride ion from cycloheptatriene derivatives.

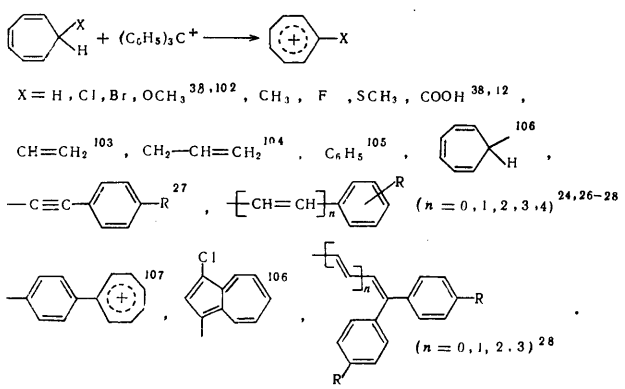
a. In the method of Kursanov and Vol'pin[98] the hydride ion is removed from cycloheptatriene and its derivatives with phosphorus pentachloride in an inert solvent. Salts of methyltropylium[98,99], and ethyl- and benzyl-tropylium[99]‡ ions have been obtained by this method from the 7-substituted cycloheptatrienes:



where R = H, CH_3, C_2H_5, and $CH_2C_6H_5$.

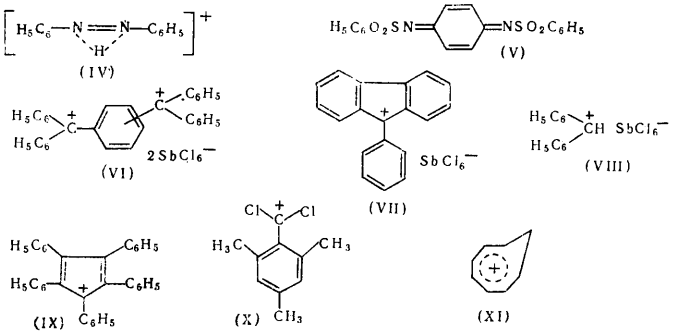
Salts of methoxy- and ethoxy-tropylium ions were obtained in the reaction of phosphorus pentachloride with 1-, 2-, and 3-alkoxycycloheptatriene[100]. When phosphorus pentachloride acts on 7-alkoxycycloheptatriene, the latter decomposes with formation of salts of the unsubstituted tropylium ion (cf. the results of Vol'pin and Akhrem[101]).

b. In Dauben's method[38] the hydride ion is removed from cycloheptatriene and its derivatives by the triphenylmethyl cation which results in the formation of triphenylmethane and an unsubstituted or substituted tropylium ion, which is a more stable carbonium ion than the triphenylmethyl cation:



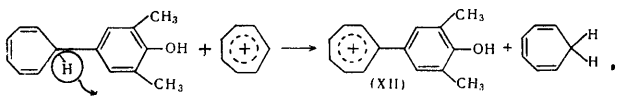
‡ The salts of ethyl- and benzyl-tropylium ions were not isolated in a pure form; a suspension of these salts in methylene-chloride was introduced directly into further reactions.

The following new acceptors have been used in recent years for the removal of the hydride ion from cycloheptatriene: protonated azobenzene (IV)[108,109], benzoquinones[110] and their derivatives, for example *p*-benzoquinone-dibenzenesulphonimide (V) in the presence of boron trifluoride-ether[47] and a number of stable carbonium ions synthesised for the first time, i.e. (VI)[111], (VII)[112], (VIII)[113], (IX)[114], (X)[115], and (XI)[87]:



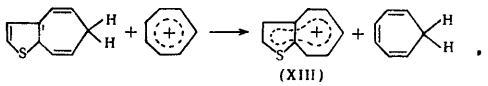
(IV) (V) (VI) (VII) (VIII) (IX) (X) (XI)

c. The removal of the hydride ions from cycloheptatriene derivatives under the action of the tropylium ion. In this case salts of a substituted tropylium ion more stable than those of the unsubstituted tropylium ion are formed. The 3,5-dimethyl-4-hydroxyphenyltropylium cation (XII)[116]:



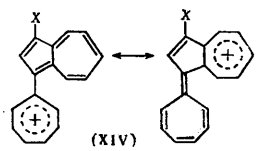
(XII)

the thenotropylium cation (XIII)[31]:



(XIII)

and the salts (XIV*a*) and (XIV*b*)[117]:

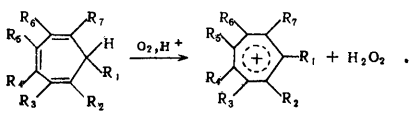


(XIV)

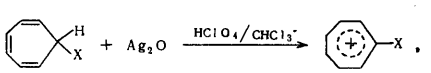
(X = H in *a* and X = C_7H_7 in *b*) were obtained in this way.

4. The oxidation of cycloheptatriene and its derivatives.

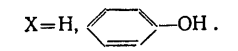
a. ter Borg et al.[118] showed that the oxidation of cycloheptatriene with atmospheric oxygen in acetic acid in the presence of perchloric or fluoroboric acids results in the formation of the tropylium ion in 30–70% yield. They suggest that substituted tropylium salts be obtained in a similar way[119]:



b. Nozoe[120] described the preparation of the tropylium and hydroxyphenyltropylium ions in the oxidation of cycloheptatriene and 4-cycloheptatrienylphenol respectively with silver oxide in chloroform solution in the presence of perchloric acid:

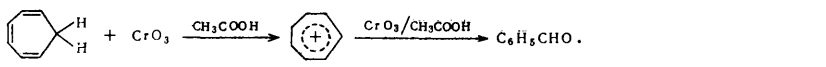


where

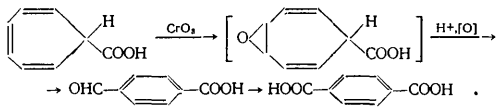


c. The oxidation of 7-cycloheptatrienecarboxylic acid (XV) with lead tetra-acetate, acid potassium permanganate, $Na_2S_2O_8$, $(NH_4)_2Ce(NO_3)_6$, and periodic acid also leads to the formation of the tropylium ion; in some cases benzaldehyde, benzyl alcohol, and terephthalic acid are formed at the same time[121].

In neutral and alkaline media potassium permanganate oxidises the acid (XV) to benzaldehyde and terephthalic acid. Doering showed that benzaldehyde forms in the oxidation of cycloheptatriene with chromic acid[9]. It also forms in the oxidation of the tropylium ion with chromic acid. On the basis of these data, Doering suggested that the oxidation of cycloheptatriene to benaldehyde takes place with the intermediate formation of the tropylium ion:



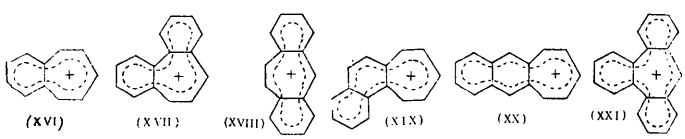
Juppé and Wolf[122] confirmed this reaction mechanism, by oxidising with chromic acid cycloheptatriene labelled with carbon-14 in the methylene group. They found that the benzaldehyde produced contains 6/7 of the label in the benzene ring. Dewar's ideas about the mechanism of the oxidation of cycloheptatriene-7-carboxylic acid to benzyl alcohol and benzaldehyde are consistent with Doering's hypotheses, but he proposes a different mechanism for the oxidation of the acid (XV) to terephthalic acid[121]:



By oxidising cycloheptatriene with chromic anhydride in pyridine, Nozoe and coworkers obtained tropone[123]. The latter also forms in the interaction of the tropylium ion with the same oxidising agent. Using his own data and also the oxidation data described above, Nozoe was able to elucidate the mechanism of the oxidation of cycloheptatriene with intermediate formation of the tropylium cation.

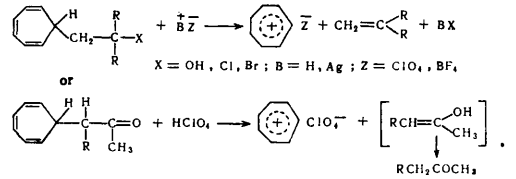
5. Heterolytic dissociation of the bonds C–O, C–C, C–N, and C–S.

a. The C–O bond in tropylium ethers[2] and tropylium-carbinols is readily ruptured under the action of acids with formation of unsubstituted tropylium salts. When acids were allowed to act on the corresponding carbinols, benzotropylium (XVI)[15], dibenzo[*a*, *c*]tropylium (XVII)[16], dibenzo[*a*, *e*]tropylium (XVIII)[17], naphtho[2,1-*a*]tropylium (XIX)[18], naphtho[2,3-*a*]tropylium (XX)[16], and tribenzo[*a*, *c*, *e*]tropylium (XXI)[19] cations were obtained. The carbinols were produced by the reduction of the corresponding tropones with lithium aluminium hydride.

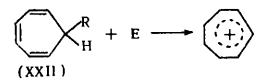


(XVI) (XVII) (XVIII) (XIX) (XX) (XXI)

b. Under the action of electrophilic agents, the C–C bond in compounds with a carbonium centre in the β-position with respect to the cycloheptatrienyl residue may dissociate[3,124]:



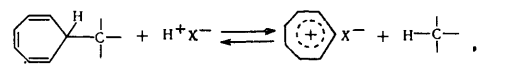
Recently Vol'pin and Akhrem showed[101] that this reaction is more general and is characteristic of cycloheptatriene derivatives with electron-acceptor substituents in the side-chain. Thus cycloheptatrienylmalonic acid (XXII*a*), cycloheptatrienylacetylacetone (XXII*b*), cycloheptatrienylacetaldehyde (XXII*c*) and cycloheptatrienylacetoacetic ester (XXII*d*) are cleaved by a wide variety of electrophilic agents E with formation of the tropylium ion:



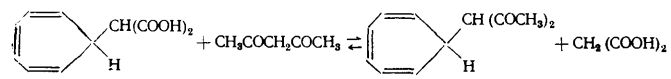
(XXII)

R = $CH(COOH)_2$ (*a*), $CH(COCH_3)_2$ (*b*), CH_2CHO (*c*), and $CH_2COOC_2H_5$ (*d*); E = Br_2, HCl(gas), HBr(gas), H_2SO_4, CH_3COOH, H_3PO_4, PCl_5, $(CH_3CO)_2O$, $(C_6H_5)_3C^+$, t-C_4H_9Br, $ZnCl_2$, and $FeCl_3$.

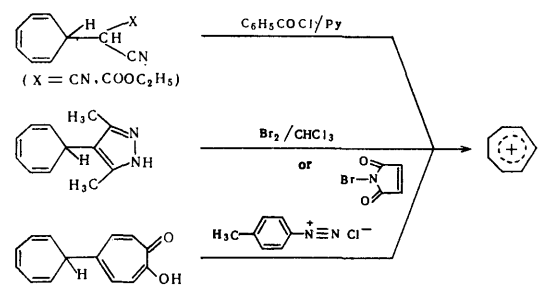
The authors suggested that this cleavage reaction is the reverse of the "tropylation" process[125]:



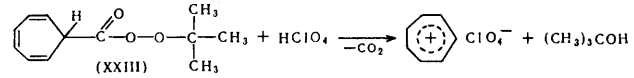
and confirmed this by the "transtropylation" reaction, which consists in the migration of the cycloheptatrienyl residue from one compound with a mobile hydrogen atom to another, for example,



Other examples of the dissociation of the C–C bond in cycloheptatriene derivatives with formation of the tropylium ion may be quoted[126–128]:

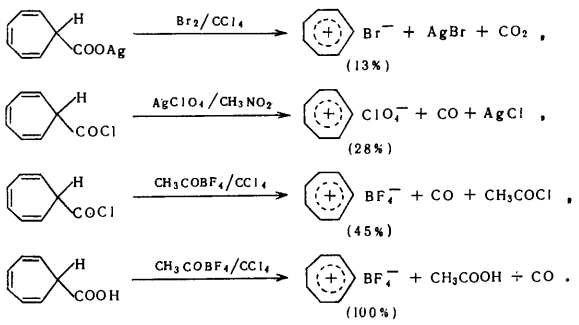


The tendency of cycloheptatriene to form the aromatic tropylium system is so great that under the action of a strong acid the C–C bond dissociates heterolytically even in the peroxide (XXIII)[129]:

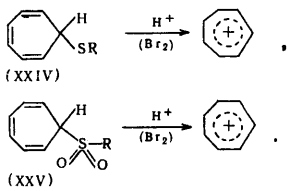


The following reactions of cycloheptatriene-7-carboxylic acid and its derivatives, proposed by Dewar and Ganellin[94]

for the preparation of tropylium salts, may be included among processes involving the dissociation of the C–C bond in cycloheptatriene derivatives:



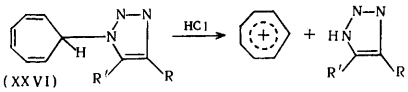
c. The C–S bond in thioethers (XXIV) and sulphones (XXV) of cycloheptatriene readily dissociates with formation of the tropylium ion under the action of acids, for example hydrobromic and perchloric acids or bromine in acetic acid[130,131]:



d. Doering showed, using ditropylurea as an example, that the C–N bond can also dissociate heterolytically with formation of the tropylium ion under the action of an acid[132]:

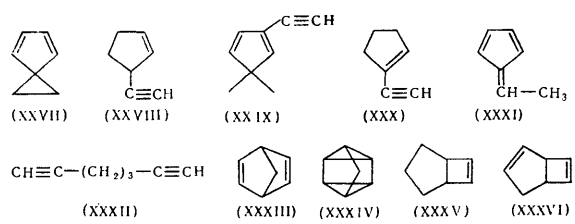


Recently Looker[133] described yet another case of the heterolysis of the C–N bond in cycloheptatriene derivatives (XXVI)[133]:



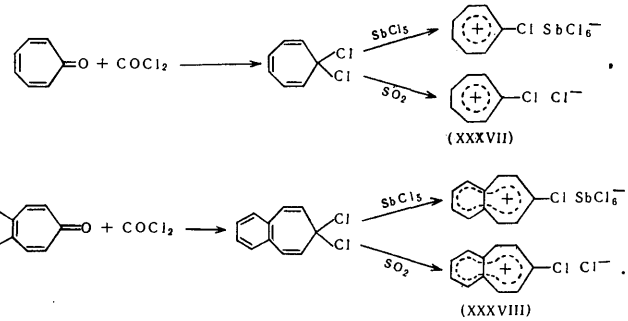
where R = R′ = $COOCH_3$, R = R′ = COC_6H_5 and R = CHO and R′ = H.

6. The formation of the tropylium ion in the mass spectrometer. Earlier it was shown that various alkylbenzenes form the tropylium ion on collision with electrons in the mass spectrometer[134]. In recent years a number of investigators have shown that benzyl chloride, benzyl alcohol[135], the isomeric C_7H_8 hydrocarbons (XXVII)–(XXXIV), cycloheptadiene, Δ^6-bicyclo[3,2,0]heptene (XXXV), and $\Delta^{2,6}$-bicyclo[3,2,0]heptadiene (XXXVI)[136–139] also have identical mass spectra:

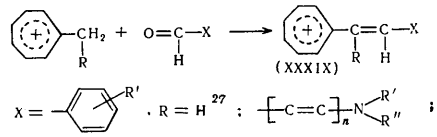


7. Other methods.

a. Föhlisch et al.[140] obtained the chlorotropylium (XXXVII) and 5-chloro-1,2-benzotropylium (XXXVIII) ions by the action of phosgene on tropone in sulphur dioxide or by further treatment with antimony pentachloride of the covalent dichloro-derivatives formed:

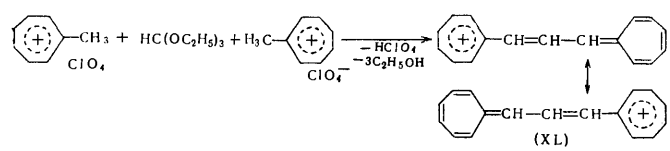


b. When methyl-, ethyl-, and benzyl-tropylium salts were condensed with aromatic aldehydes and their derivatives in acetic acid solution containing a small amount of perchloric acid, the following substituted tropylium compounds (XXXIX) were obtained:

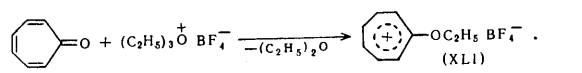


R = H, CH_3, and C_6H_5§ [38]; n = 0 and 1; X = 1-naphthyl, 2-naphthyl, 9-phenanthryl, 9-anthryl, and 3-pyrenyl; R = H.[29]

Hafner and coworkers obtained the salt (XL) by the condensation of the methyltropylium ion with orthoformic ester[141]:



By allowing tropone to react with triethyloxonium fluoroborate, they obtained ethoxytropylium fluoroborate (XLI):

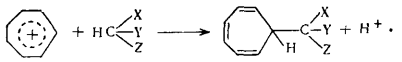


2. The Properties of the Tropylium Ion

The studies on the reactivity of the tropylium ion have continued in recent years. The most important property of the tropylium ion, as a carbonium ion, is its electrophilicity (see Section II). The tropylation reaction discovered by Vol'pin et al.,[142] i.e. the replacement of a mobile

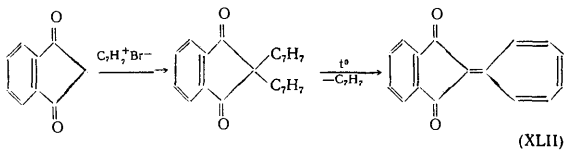
§ The interaction of methyl-, ethyl-, and benzyl-tropylium salts with N-substituted formamides and β-(dialkylamino) acrolein derivatives with formation of immonium salts takes place in the presence of phosphorus oxychloride.

hydrogen atom by the cycloheptatrienyl residue, is associated with the electrophilic properties of the tropylium ion:

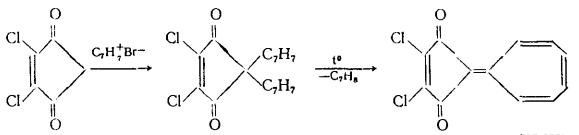


This reaction has found extensive application in the synthesis of cycloheptatriene derivatives.

Thus Jordan and Elliott [143] introduced the seven-membered ring into the molecules of 2-ethoxycarbonylcyclopentanone, potassium phthalimide, and indane-1,3-dione; Nozoe and coworkers introduced the seven-membered ring into β-naphthol [144] and tropolone [128], and Hafner [117] and later Anderson [106] "tropylated" azulene. Kitahara and coworkers obtained quinones of the sesquifulvalene series, (XLII) and (XLIII), with the aid of the tropylation reaction [145]:



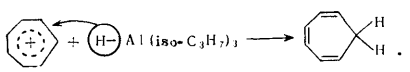
(XLII)



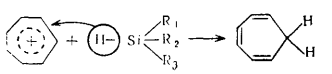
(XLIII)

Further examples of the reaction of tropylium ions in which a double bond is activated by electron-donor substituents, first observed by Vol'pin et al. [142,146], have been discovered [28,147].

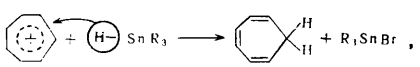
The tropylium ion as an acceptor of hydride ions has been used for the further study of hydride migrations. It has been shown that the tropylium ion can remove a hydride ion not only from complex alkali metal hydrides but also from simple aulminium hydrides [32]:



It has been found that the Si–H and Sn–H bonds can also dissociate heterolytically under the action of the tropylium ion [32,148]:

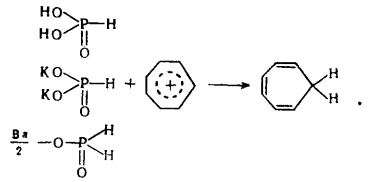


where $R_1 = R_2 = R_3 = C_2H_5$ and $R_1 = H$, $R_2 = CH_3$, and $R_3 = C_2H_5$.

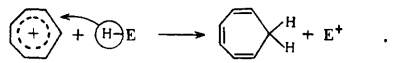


where $R = C_2H_5$ and C_6H_5.

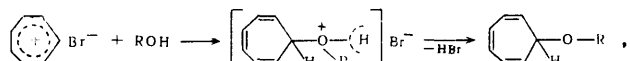
The study of the dissociation of the P–H bond under the action of the tropylium ion proved to be particularly interesting. Examples of both homolytic [149] dissociation of the P–H bond and ionic dissociation with the removal of a proton were known earlier [150]. Recently it has been shown that phosphorous acid, potassium phosphite, and barium hypophosphite in aqueous solution reduce the tropylium ion with formation of cycloheptatriene [10]:



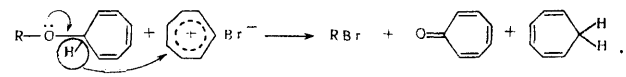
Thus it has now been demonstrated that heterolysis of an E–H bond with removal of a hydride ion under the action of the tropylium ion is in principle possible for elements of Groups I, III, IV, and V:



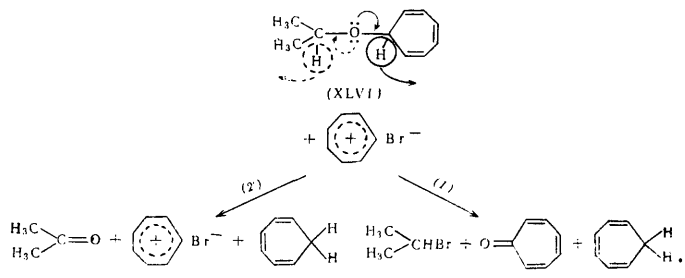
Systematic study of the interaction of the tropylium ion with alcohols has shown that the ion reacts with primary, secondary, and tertiary alcohols [151]. In the reaction with primary and tertiary aliphatic alcohols the first step is the formation of the hydroxonium compound (XLIV), which readily loses a proton with formation of the alkyl tropyl ether (XLV). The alkyl tropyl ether interacts with a second molecule of the tropylium salt. The tropylium ion then removes a hydride ion from the cycloheptatriene ring with formation of cycloheptatriene, tropone, and the alkyl halide:



(XLIV) (XLV)

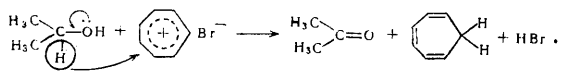


In the reaction with a secondary aliphatic alcohol, in particular isopropyl alcohol, acetone forms in addition to cycloheptatriene, tropone, and isopropyl bromide. The formation of acetone can be explained by the fact that in the reaction of the intermediate isopropyl tropyl ether (XLVI) with the tropylium ion a hydride ion may be removed not only from the cycloheptatriene ring (1) but also from the isopropyl group (2):



(XLVI)

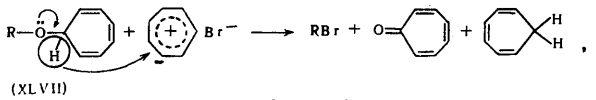
The authors showed that in the reaction between isopropyl ether and tropylium bromide a hydride ion is indeed removed both from the isopropyl group and from the cycloheptatrienyl ring. However, one cannot exclude the possibility of the direct removal of the hydride ion by the tropylium ion from the isopropyl alcohol molecule:



The occurrence of this process in the overall reaction can also be expected on the basis of the relatively large hydride mobility of the hydrogen atom in the CH group of isopropyl alcohol[152-156]. Similar considerations can also be used to explain the reaction between benzyl alcohol and the tropylium ion[32], as a result of which tropone is formed together with benzaldehyde and cycloheptatriene.

The high hydride mobility in alkyl tropyl ethers was suggested by the authors by analogy with the high hydride mobility of the hydrogen atom in ditropyl ether. Ter Borg and coworkers[157] and Nozoe and coworkers[158] showed that ditropyl ether is capable of interacting with the tropylium ion to form cycloheptatriene and tropone, catalytic amounts of the tropylium ion being sufficient for the reaction to occur[159].

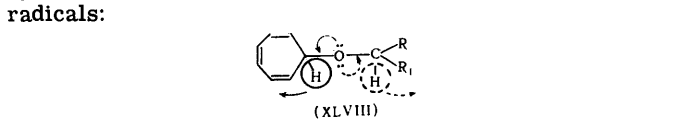
Alkyl tropyl ethers also react with the tropylium ion. In the reaction of methyl tropyl, n-propyl tropyl, and t-butyl tropyl ethers (XLVII) with the tropylium ion cycloheptatriene, tropone, and alkyl halides are formed. This is consistent with the hypothesis of the removal of a hydride ion from the seven-membered ring:



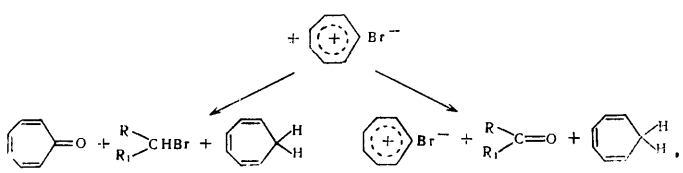
(XLVII)

where R = CH_3, n-C_3H_7, and t-C_4H_9.

The reaction of isopropyl tropyl and benzyl tropyl ethers (XLVIII) with the tropylium ion results in the formation of acetone and benzaldehyde in addition to cycloheptatriene, tropone, and isopropyl and benzyl bromides. Thus in these processes a hydride ion is removed both from the cycloheptatriene ring and from the isopropyl and benzyl radicals:

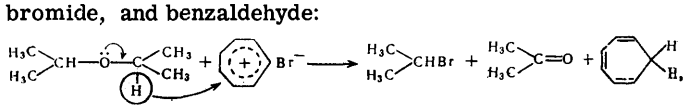


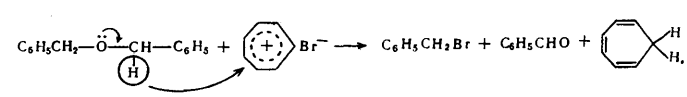
(XLVIII)



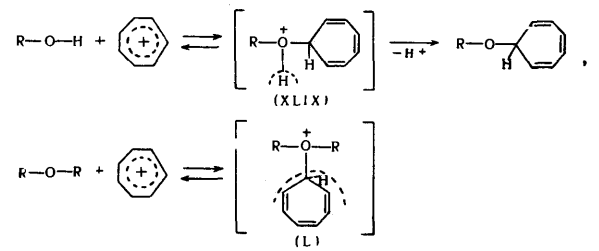
where R = R_1 = CH_3 and R = H and R_1 = C_6H_5.

In the study of the interaction of the tropylium ion with ethers the same workers found that bisprimary aliphatic ethers are incapable of interacting with the tropylium ion[160]. Di-isopropyl and dibenzyl ethers do react with the tropylium ion. A hydride ion is then removed directly from the ether molecule. The reaction with di-isopropyl ether yields cycloheptatriene, isopropyl bromide, and acetone and that with dibenzyl ether yields cycloheptatriene, benzyl bromide, and benzaldehyde:





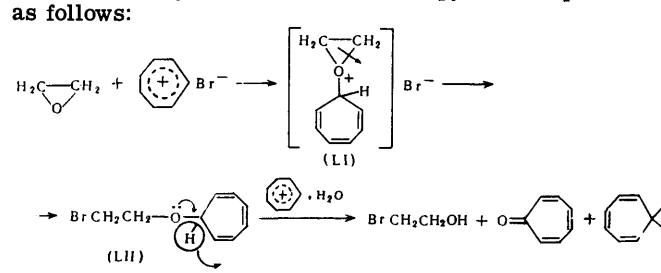
Thus the mechanism of the interaction between the tropylium ion and ether is different from that of its interaction with alcohols. The explanation is probably that in the interaction between alcohols and the tropylium ion hydroxonium compounds (XLIX) are formed, which, on losing a proton, are converted into alkyl tropyl ethers. In their reaction with the tropylium ion ethers can form the oxonium salts (L), which on decomposition most readily split off the tropylium ion, as the most stable carbonium ion, the initial ether being regenerated:



(XLIX)

(L)

However, the same workers found an example of the reaction[161] in which the ether interacts with the tropylium ion with the intermediate formation of an alkyl tropyl ether. The ether involved in this process is ethylene oxide. The reaction of ethylene oxide with the tropylium ion proceeds as follows:

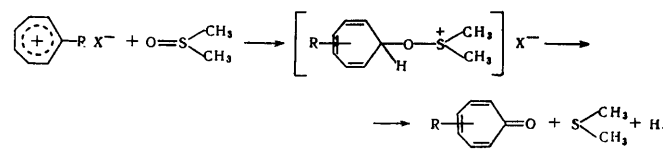


(LI)

(LII)

The C–O bond in the intermediate oxonium compound (LI) readily dissociates as a result of the high strain in the three-membered ring. The β-bromoethyl tropyl ether (LII) was isolated and identified and it was shown that cycloheptatriene, tropone, and ethylene bromohydrin are formed in its reaction with tropylium bromide.

In conclusion one more reaction, which we believe to be of interest, should be mentioned. Kitahara and Funamizu found[162] that tropone is formed in the reaction between the tropylium ion and dimethyl sulphoxide:



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SYNTHESIS OF SUBSTITUTED INDOLES VIA INDOLINES

M. N. Preobrazhenskaya

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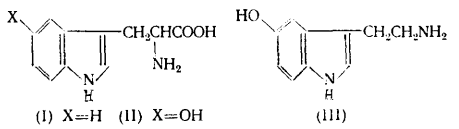
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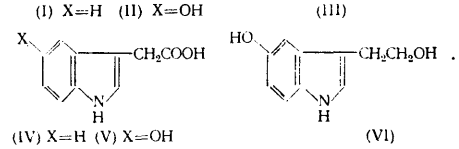
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I. INTRODUCTION

Indole derivatives play an important role in vital processes [1,2]. Of special importance are the essential amino-acid tryptophan (I) and the products of its metabolism, for example, 5-hydroxytryptophan (II), serotonin (III), 3-indolylacetic (IV) and 5-hydroxy-3-indolylacetic (V) acids, 5-hydroxytryptophol (VI) and a number of other substances:

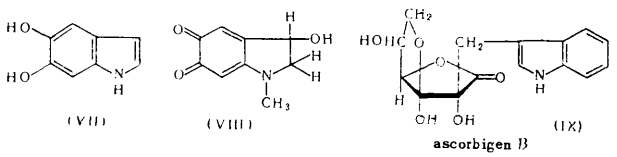


(I) X=H (II) X=OH (III)



(IV) X=H (V) X=OH (VI)

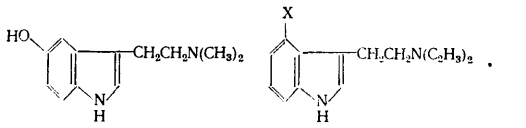
The structure of 5,6-dihydroxyindole (VII) is the basis of the animal pigment melanin [3]. The processes involved in the biosynthesis of melanin are closely related to the metabolism of aminocatechols, including adrenalin and tyrosine. One of the products of adrenalin metabolism is adrenochrome (VIII) [4]. It has been shown recently [5] that ascorbic acid in plants exists in a bound form as two diastereoisomeric ascorbigens A and B (IX):



(VII) (VIII) (IX)

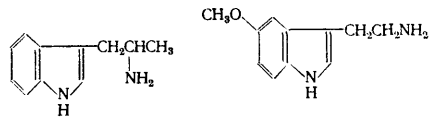
ascorbigen B

Many compounds containing the indole ring exhibit high pharmacological activity. It is sufficient to recall reserpine and other Rauwolfia alkaloids, lysergic acid, brucine, yohimbine, eserine, and other alkaloids, and also halucinogenic compounds such as bufotenin (X) (a component of frog venom), psilocin (XI), psilocybin (XII), and others [1].



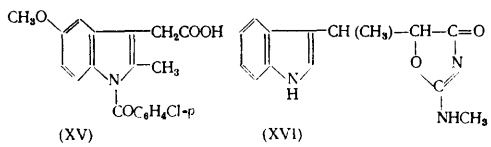
(X) (XI) X=OH (XII) X=OPO_3H_2

The synthetic research on pharmacologically active compounds in the indole series has proved extremely fruitful. In particular, valuable medicinal substances have been found—indopane [6] (3-indolylisopropylamine) (XIII), used as a stimulating antidepressant in psychiatry and mexamine (5-methoxytryptamine) (XIV) [7], used in the prophylaxis of radiation damage:



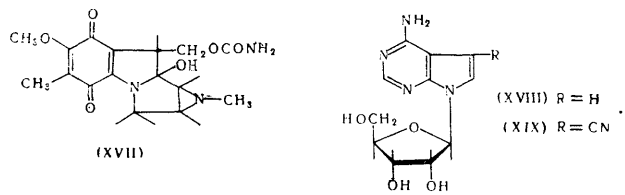
(XIII) (XIV)

Considerable interest was aroused by the discovery of indole derivatives with high anti-inflammatory activity, among which the most important is indomethacin—1-(*p*-chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid (XV) [8]:



(XV) (XVI)

Until recently indole derivatives with high antimicrobial activity were unknown. However, the first communication dealing with the antibiotic indolmycin (XVI), which inhibits the development of strains of *Staphylococcus aureus*, a micro-organism resistant to the most widely used antibiotics, appeared in 1961. [9,10] Vigorous studies are being made on the synthesis of the antibiotic mitomycin (XVII) and related compounds which exhibit high cytostatic, bacteriostatic, and fungicidal activity [11,12]:



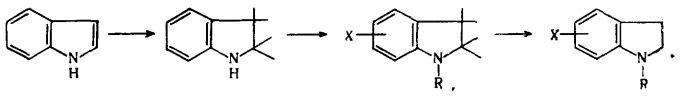
(XVII) (XVIII) R = H (XIX) R = CN

The reports of the discovery of a new group of antibiotics, tubercidin (XVIII) and toyokamycin (XIX) [13], are extremely interesting. These compounds are based on the 5,7-diazaindole (pyrimidinopyrrole) structure.

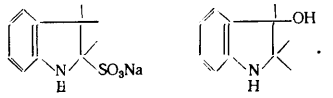
The structure of many indole compounds is based on tryptophan, indole-3-acetic acid, or tryptamine (3-indolylethylamine). In this connection methods of synthesising the side-chain in position 3 of the indole ring have been developed in special detail. The method of introducing substituents in position 1 have been investigated much less,

although many 1-substituted indoles are of great interest—for example, indomethacin (XV), tubercidin (XVIII), and others. The reason for the difficulty of introducing substituents in position 1 of the indole system is that the NH group exhibits acid rather than basic properties, as a result of which direct *N*-alkylation or *N*-acylation of indole frequently cannot be achieved. Mercury or silver salts (with one organic anion) of the type N–M, which are widely used for synthetic purposes, for example in the purine series, have not been described for indoles. Magnesium, sodium, and lithium derivatives of indole usually react with the formation of C_2 or C_3 derivatives. Serious difficulties are also encountered in attempts to introduce substituents into the benzene ring of the indole system. Under the conditions of an electrophilic substitution reaction, most indole derivatives decompose or react in different ways simultaneously. The classical methods of synthesis (the Fischer, Reissert, and other syntheses), in which the molecule is synthesised from components already containing definite substituents, frequently prove cumbersome or altogether inapplicable to indoles with substituents in the benzene ring.

A method based on temporary exclusion of the pyrrole ring has been proposed for the introduction of substituents into the indole ring[14–16]. Indole is converted into 2,3-dihydroindole (indoline), which is an aromatic amine and can be made to undergo various electrophilic reactions with formation of indoline derivatives substituted both in the benzene ring and at the nitrogen atom. Dehydrogenation of these derivatives yields the substituted indole. Thus instead of using unstable, readily decomposed, and difficult to isolate indole derivatives, the experiments are performed with indolines, which are aliphatic-aromatic amines:



Instead of dihydroindole, one can use in this reaction also the unstable adduct of indole and sodium bisulphite, the sodium salt of indoline-2-sulphonic acid (XX), which also exhibits the properties of an aromatic amine[17]. Conversion into indole derivatives is achieved by treatment with alkali:



(XX) (XXI)

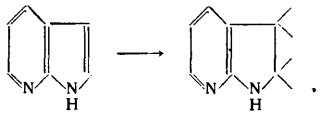
In many cases indolines cannot be obtained from the corresponding indole derivatives and they are synthesised in other ways. This applies, for example, to 2,3-dihydro-3-hydroxyindole, 3-indolinol (XXI), which is readily substituted and forms indole derivatives on dehydration[18]. In this connection, intensive studies have been made in recent years on the methods of synthesis of various indoline derivatives from hydroxyindoles, isatins, and various aromatic compounds.

This review deals with the methods of synthesis of indolines, the substitution reactions in the indoline series, and methods of conversion into the corresponding substituted indoles.

II. METHODS OF PREPARATION OF INDOLINES†

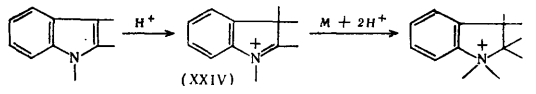
1. Preparation of Indolines by the Reduction of the Corresponding Indoles

The most convenient method for the preparation of indoline is hydrogenation of indole over Raney nickel at 80–100 atm and 75–150°C in an alcoholic or dioxan solution[19]. Further temperature rise leads to the formation of octahydroindole; in alcoholic solution the process is accompanied by *N*-alkylation[20,21]. The method is suitable for the preparation of substituted indolines[22,23]. A series of indolines were obtained by hydrogenation over copper chromite at 250–300 atm and 170–190°C.[24–26] The hydrogenation of indole derivatives over PtO_2 in an alcohol–HBF_4 mixture at 1 atm and room temperature has also been described[27]. The hydrogenation of pyridinopyrrole, 7-azaindole (XXII), to the 2,3-dihydro-derivative (XXIII) is carried out over a nickel catalyst at 200°C and 100 atm. An increase of temperature results in cleavage of the pyrrole ring[28,29]:



(XXII) (XXIII)

1-, 2-, or 3-alkylindoles can be reduced to the corresponding dihydro-derivatives under the action of zinc or tin in hydrochloric acid[30–35]. The ease of reduction of indoles to 2,3-dihydro-derivatives in an acid medium, associated with the formation of the indolenine structure (XXIV) as a result of the protonation of indoles in position 3, is striking[36,37].



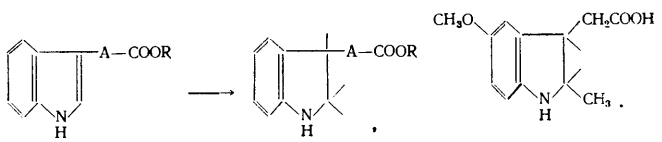
(XXIV)

However, in the reduction of unsubstituted indole in hydrochloric acid it is impossible to isolate indoline, because dimerisation and trimerisation products form under these conditions. In the reduction of indole with zinc in 85% phosphoric acid at 70–80°C in a stream of nitrogen it is possible to avoid the polymerisation of indole and to obtain indoline in 64–69% yield[38]. 2,3-Dimethylindole, 1,2,3,4-tetrahydrocarbazole, and its *N*-methyl derivatives have been synthesised under the same conditions. It has been shown that in the reduction of 2,3-dimethylindole with tin in hydrochloric acid the *cis*- and *trans*-isomers‡ are formed in proportions of 3 : 2,[25] and in the reduction with zinc in 85% phosphoric acid the proportions are 65 : 35.[38] In hydrogenation over copper chromite only the *trans*-isomer is formed[25]. In many cases it is possible to reduce the 1-substituted indoles to indolines under the action of lithium aluminium hydride in tetrahydrofuran[40,41]. Electrochemical reduction of indole[42] and reduction of indole with diborane[43] have been described.

† The synthesis and properties of 2,2- or 3,3-disubstituted indolines, which cannot be converted into the corresponding indoles without the rupture of a C–C bond, will not be considered.

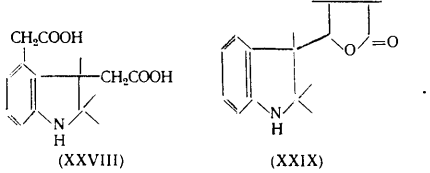
‡ Studies on the *cis-trans*-isomers of 2,3-dimethylindoline have been described by Anet and Muchowski[39].

It is of very great interest to carry out the conversion indole → indoline → substituted indoline → substituted indole using compounds containing the $CH_2CH_2NR_2$ or $(CH_2)_nCOOH$ residue in position 3 of the indole ring. Such conversions have been achieved for indole-3-alkanoic acids[44,45]. 2,3-Dihydroindole-3-propionic (XXVI, A = CH_2CH_2) acid was obtained by dehydrogenation of a salt of indole-3-propionic acid (XXV, A = CH_2CH_2) over Raney nickel at room temperature and 250 atm.[14] Esters of 2,3-dihydroindole-3-propionic [and -3-butyric? (Ed. of Translation)] acids (XXVI, A = CH_2CH_2 or CH_2CHCH_3) have also been obtained under these conditions[46]. The potassium salt of indole-3-acetic acid (XXV, A = CH_2) has been hydrogenated over Raney nickel at 100°C and 70 atm in order to obtain the dihydro-derivative[44]. 5-Methoxy-2-methylindole-3-acetic acid (XXVII), the starting material for the synthesis of indomethacin (XV), has been obtained under the same conditions[47]:



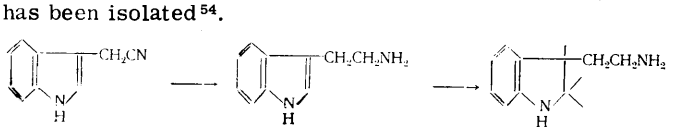
(XXV) (XXVI) (XXVII)

The disodium salt of indole-3,4-diacetic acid has been hydrogenated over Raney nickel at 80°C and 100 atm and the corresponding indoline diacid (XXVIII) has been obtained[48]:



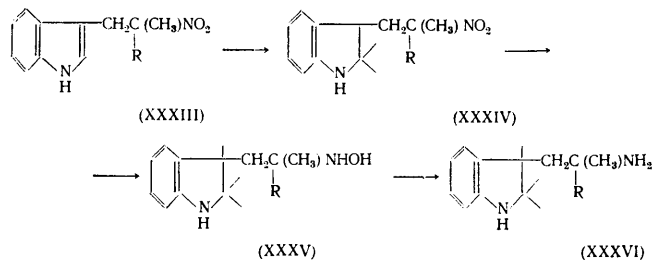
(XXVIII) (XXIX)

The conversion of esters of indole-3-alkanoic acids into the 2,3-dihydro-derivatives by hydrogenation over platinum oxide at the normal pressure and room temperature has been described[49,50]. The ester of 5-methoxy-2-methylindoline-3-acetic acid (XXVII) has been obtained under the action of tin in hydrochloric acid[51]. There is no information about the reduction of amino- and hydroxy-acids of the indole series, with the exception of the reduction of γ-(indol-3-yl)-γ-oxobutyric acid into indolinylbutyrolactone (XXIX)[52]. The data on 2,3-dihydro-5-hydroxytryptophan as well as the information on 2,3-dihydro-5-hydroxytryptamine (dihydroserotonin) appears to be unreliable[53]. The reduction of tryptamines to 2,3-dihydrotryptamines has been almost not investigated. Tryptamine (XXXI) forms in the hydrogenation of indole-3-acetonitrile (XXX) over Raney nickel at room temperature and 90 atm, an increase of temperature to 100°C resulting in partial conversion of tryptamine into dihydrotryptamine (XXXII), whose dipicrate has been isolated[54].



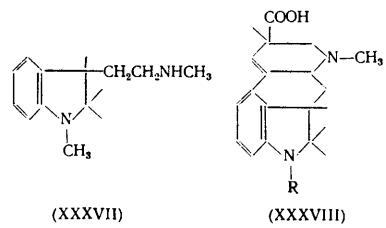
(XXX) (XXXI) (XXXII)

In the hydrogenation of 3-nitroisopropylindole (XXXIII, R = H) over PtO_2 in alcoholic hydrochloric acid it proved possible to obtain the dihydro-derivatives (XXXIV, R = H) and (XXXV, R = H) and on further hydrogenation 3-amino-isopropyl-2,3-dihydroindole (XXXVI, R = H)[55]:



(XXXIII) (XXXIV) (XXXV) (XXXVI)

3-Nitroisobutylindoline (XXXIV, R = CH_3) has been obtained similarly from 3-nitroisobutylindole (XXXIII, R = CH_3). Octahydroindole derivatives are formed together with these substances[55]. The pyrrole ring is reduced more readily than the nitro-group as a result of the easier reduction of the corresponding indolenine structure formed in an acid medium. The introduction of a methyl group into the pyrrole ring of the tryptamine molecule facilitates, as for indolealkanoic acids, the reduction of the double bond in the pyrrole ring. *NN'*-dimethyltryptamine can be converted into the dihydro-derivative (XXXVII) by zinc in hydrochloric acid[56]:

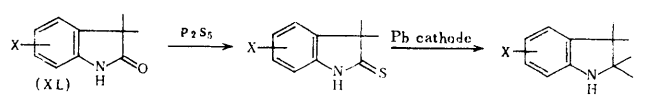


(XXXVII) (XXXVIII)

The conversion of lysergic acid derivatives into dihydrolysergic acid derivatives (XXXVIII) has been achieved similarly[57].

2. Syntheses of Indoline Derivatives Based on Isatins, Indoxyls, and Hydroxyindoles

The direct electrolytic reduction of isatin and hydroxyindole into indoline has been described[58]. It is more convenient to obtain indoline (XXXIX) from hydroxyindoles (XL) via mercaptoindoles (XLI)[59,60]:

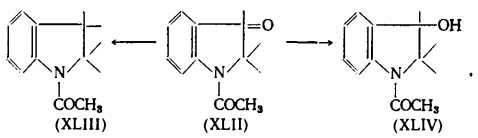


(XL)

where X = H, 4-CH_3O, and 6-CH_3O.

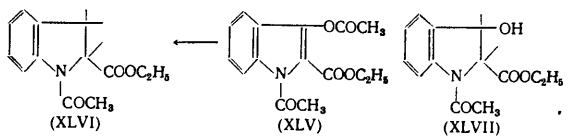
A mixture of indoles and indolines (with the indoles predominating) is usually formed in the reduction of *N*-substituted hydroxyindoles with lithium aluminium hydride[40,61-65]. The hydroxyindole unsubstituted at the nitrogen atom cannot be converted either into indole or indoline by the action of lithium aluminium hydride[40]. The formation of a certain amount of 1-alkylindolines in the reduction of 1-alkylhydroxyindoles with lithium aluminium hydride can probably be accounted for by further reduction of the 1-alkylindoles formed. The reduction of hydroxyindole derivatives with diborane leads to a mixture of the corresponding indoles and indolines[43], but this reaction does not appear to be of preparative value.

Depending on the reaction conditions, 1-acetylindoline (XLIII) or 1-acetyl-3-hydroxyindoline (XLIV) are formed in the catalytic reduction of 1-acetylindoxyl (XLII)[66,67]:



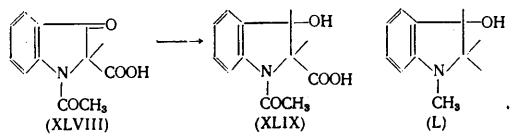
(XLIII) (XLII) (XLIV)

The hydrogenation of *ON*-diacetylindoxyl at 100 atm and 90°C over a nickel catalyst results in the formation of 1-acetylindoline in 90% yield, and from the reaction performed under milder conditions it is possible to isolate 1-acetyl-3-hydroxyindoline (10% yield). In the hydrogenation of 3-acetoxy-1-acetyl-2-ethoxycarbonyl indole (XLV) over Raney nickel at 85 atm and 110°C the product was an ester of 1-acetylindoline-2-carboxylic acid (XLVI) and at 60 atm and 60°C an ester of 1-acetyl-3-hydroxyindoline-2-carboxylic acid (XLVII)[68]:



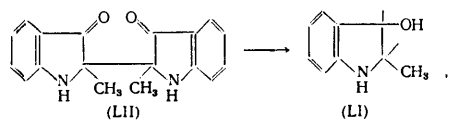
(XLVI) (XLV) (XLVII)

It proved possible to achieve the same reaction in the hydrogenation of an ester of 1-acetylindoxyl-2-carboxylic acid (XLVIII) over nickel chromite at room temperature and a lower pressure[68]:



(XLVIII) (XLIX) (L)

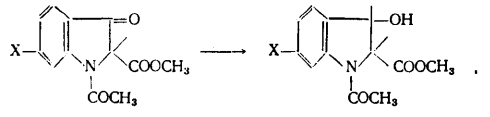
The most convenient method for the preparation of 3-hydroxyindoline is the reduction of isatin with lithium aluminium hydride (yields of 21%[70] and 14%[18]). 3-Hydroxy-1-methylindoline cannot be obtained by the reduction of 1-methylisatin. 3-Hydroxy-1-methylindoline (L) has been obtained by the methylation of 3-hydroxyindoline[71]. In the reduction of dihydroxyindole 3-hydroxyindoline is formed in 15% yield and in the reduction of indoxyl in 5% yield[72]. 3-Hydroxy-2-methylindoline (LI) has been obtained in good yield by the reduction of 2,2′-dimethyl-2,2′-di-indoxyl (LII) with $NaBH_4$ in methanol[73]:



(LII) (LI)

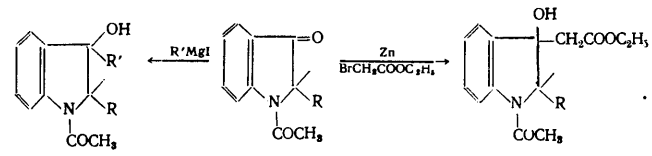
Analysis of the NMR spectrum showed that compound (LI) is a mixture of the *cis*- and *trans*-isomers in proportions of 1:4.[73]

Another example of the conversion of indoxyl derivatives (LIII) into 3-hydroxyindoline derivatives (LIV) with the aid of metal borohydrides has been described[74]:



(LIII) (LIV)

Hydroxyindoline derivatives (LVI) and (LV) have also been obtained from 1-acetyl-2-alkylindoxyls (LVII) by the Grignard and Reformatskii reactions[75]:

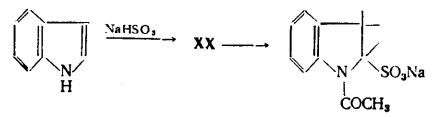


(LVI) (LVII) (LV)

In the synthesis of various indole derivatives from indoxyl, compounds whose structure is based on 3-hydroxyindoline (see, for example, Nenitzescu and Dan Raileanu[76]) are often formed as intermediates. Here only those cases are considered where these compounds have been isolated and identified.

3. Adducts of Indoles and Sodium Bisulphite and Indole Dimers

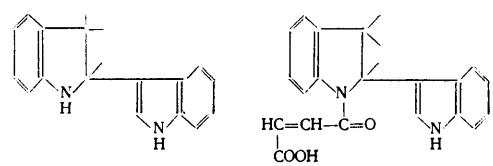
The "exclusion of the pyrrole ring" of indole can also be achieved by the conversion of indole into the sodium salt of indoline-2-sulphonic acid (XX)[17,77]:



(LVIII)

The product of the acetylation of a salt of indoline-2-sulphonic acid (LVIII) is used in electrophilic substitution reactions. The advantage of this method is the ease of preparation of the adduct (the yields are quantitative) and the ease of reconversion into indole derivatives. However, the instability of the reaction products and the impossibility of purifying and identifying the intermediates greatly reduce the value of this method.

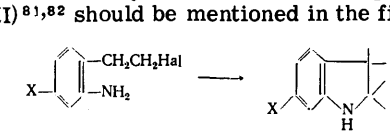
Indole dimers, which have the structure of indolinylindoles (LIX)[78,79] and the adduct of indole and maleic anhydride (LX)[80] should also be mentioned.



(LIX) (LX)

4. Synthesis of Indolines by the Closure of the Pyrroline Ring

The studies on the cyclisation of *o*-aminophenylethyl halides (LXI)[81,82] should be mentioned in the first place:

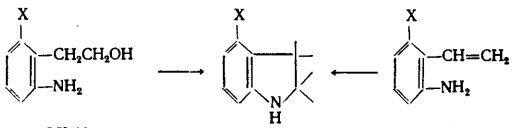


(LXI) (LXII)

where X = H, $RHNSO_2$.

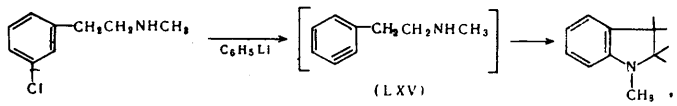
The mechanism of this reaction has not been investigated. The method has been used to prepare indoline-6-sulphonamides (LXII, X = $RHNSO_2$)[83,84]. It is particularly

valuable, since direct sulphonyl chlorination of indolines leads to 5-derivatives (see Section III). The cyclisation is achieved under the action of aqueous alkali. Indoline and its derivatives have also been obtained from *o*-aminostyrene (LXIII)[85] or *o*-aminophenylethanol (LXIV)[65,86,87]:



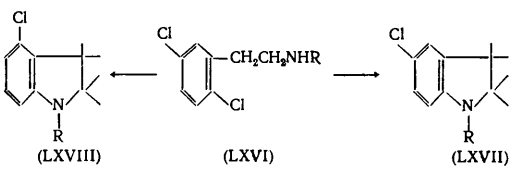
(LXIV) (LXIII)

Indolines are formed when halogeno-derivatives of β-phenylethylamine are acted upon by reagents such as C_6H_5Li, $(C_2H_5)_2NLi$, $NaNH_2$, and others. The intermediate aryne structure (LXV) is formed, this being followed by intramolecular nucleophilic addition to the triple bond of the dehydrobenzene ring[65,88,89].



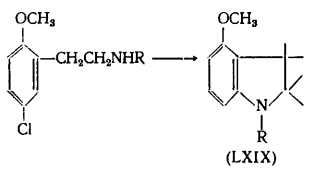
(LXV)

A halogen in a position *meta* to the side-chain forms the aryne more readily than the halogen in the *ortho*-position, which leads to higher yields of indolines when *meta*-derivatives are used. However, it proved possible to obtain 1-methylindoline from β-(*o*-chlorobenzyl)ethylmethylamine in 50% yield[90]. When the benzene ring contains halogens in positions *ortho* and *meta* to the side-chain (LXVI), a mixture of 4- and 5-halogeno-derivatives (LXVIII) and (LXVII) is formed, 4-chloroindoline (the product of the cyclisation of *m*-chlorophenylethylamine) (LXVIII) predominating considerably:



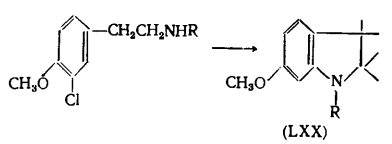
(LXVIII) (LXVI) (LXVII)

This method has been used to prepare 4-methoxyindolines (LXIX) and 6-methoxyindolines (LXX)[91]:



(LXIX)

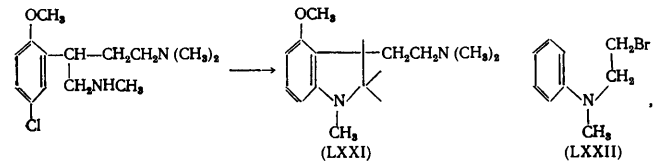
where R = H, CH_3, and $CH_2C_6H_5$;



(LXX)

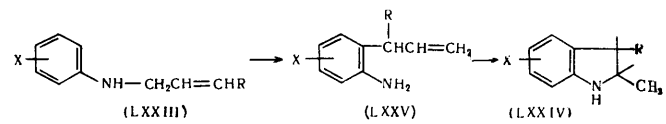
where R = H, CH_3, and C_2H_5.

4- and 6-methoxyindolines have been converted into 4- and 6-hydroxyindolines. 3-(β-Dimethylaminoethyl)-4-methoxy-1-methyl-2,3-dihydroindoline (LXXI) has also been obtained[91]:



(LXXI) (LXXII)

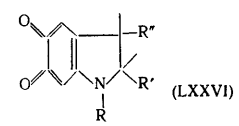
1-Methylindoline has been isolated after the reaction between aluminium chloride and (β-bromoethyl)methylaniline (LXXII)[92]. 2-Methylindolines (LXXIV) are formed (together with small amounts of 2-methylindoles) when *N*-allylanilines (LXXIII) are cyclised under the action of acid reagents[25,93]:



(LXXIII) (LXXV) (LXXIV)

where R = H and CH_3 and X = H, 7-CH_3, 5-CH_3, and 5-F. *o*-Allylaniline (LXXV) is an intermediate in this reaction[25].

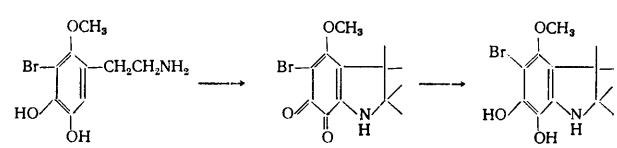
The possibility of obtaining indoline systems by the oxidation of aminocatechols should be recalled. Adrenochrome (VIII), which was isolated after adrenalin had been subjected to the action of catechol oxidase, silver oxide, and other agents[94], has already been mentioned. Aminochromes (LXXVI), analogues and derivatives of adrenochromes, have also been prepared:



(LXXVI)

Among the ether derivatives of adrenalin, the aminochromes (LXXVI, R = CH_3, R′ = H, R″ = alkoxy-group) have been obtained[95].

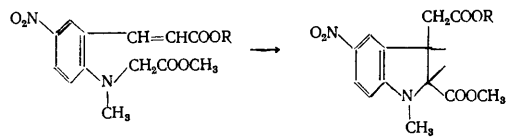
Adrenalin analogues have been prepared from 3-hydroxyindolinequinones (LXXVI, R = R′ = alkyl residues and R″ = OH)[96]. By oxidising dihydroxyphenylalanine derivatives, indolinequinonecarboxylic acids (LXXVI, R = CH_3, C_2H_5, etc., R′ = COOH, and R″ = H) were synthesised[96]. Among the phenylethylamine derivatives, the indolinequinones (LXXVI, R = CH_3, C_2H_5, etc. and R′ = R″ = H) were prepared[96]. Other compounds synthesised are aminochromes, which are indoline-6,7-*o*-quinones (LXXVII), some of which have been used in the synthesis of polyhydroxylated indolines (LXXVIII)[97]:



(LXXVII) (LXXVIII)

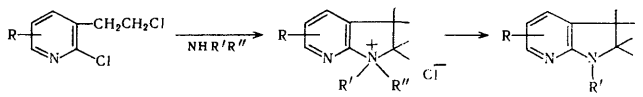
It has been shown that the action of potassiun iodate and other halogen-containing oxidising agents on adrenalin and its analogues leads to the preparation of 7-halogeno-derivatives of adrenochrome[98-100]. Adrenochrome derivatives have been used as the starting materials in the synthesis of certain indole systems.

It proved possible to close the indoline ring (LXXIX) by cyclisation under the conditions of the Michael reaction[101]:



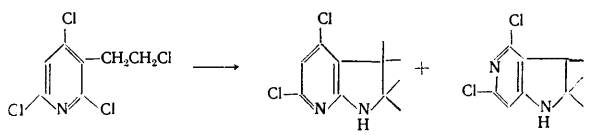
(LXXIX)

In recent years an increasing number of studies have been devoted to the methods of synthesis of pyridino- or pyrimidino-pyrroles (aza- or diaza-indolines)§. These investigations were stimulated by the discovery of the high biological activity of the aza-analogues of nucleosides and nucleotides and the discovery of new antibiotics of the type of tubercidin and toyokamycin. An especially large number of studies are concerned with the development of methods of synthesis of pyridinopyrrolines (azaindolines). It has been established that, when 3-(β-chloroethyl)pyridines containing halogen atoms in positions 2 or 4 (LXXX) are condensed at a high temperature with ammonia and primary or secondary amines, indolines (LXXXI) are formed. Using various chloropyridines and amines, it proved possible to prepare by this method more than 30 substituted 7- and 5-azaindolines[102-114]. The first stage of the reaction[105,109] is the replacement of the aromatic chlorine by the NH_2 residue, this being followed by the formation of the quaternary salt (LXXXII) and the removal of an alkyl halide:



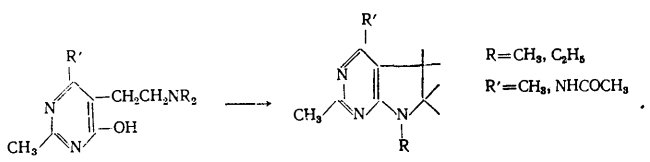
(LXXX) (LXXXII) (LXXXI)

The reaction of 2,4,6-trichloro-3-(β-chloroethyl)pyridine (LXXXIII) with amines takes place with the formation of a mixture of 5- and 7-azaindolines, (LXXXIV) and (LXXXV) respectively, in proportions of 34.6 : 42.2.[109,112] 5- and 7-indolines were obtained by the dechlorination of these compounds.



(LXXXIII) (LXXXV) (LXXXIV)

The formation of pyrimidinopyrrolines (5,7-diazaindolines) (LXXXVI) by the action of phosphorus pentachloride and then alkali on pyrimidines containing β-dialkylamino- and hydroxy-groups in the *ortho*-position (LXXXVII) has been described[115,116]:

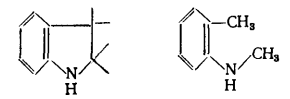


(LXXXVII) (LXXXVI)

§ The present review deals only with pyridino- and pyrimidino-pyrroles and -pyrrolines, which can be regarded as 4-, 5-, 6-, or 7-aza-analogues of indole or indoline.

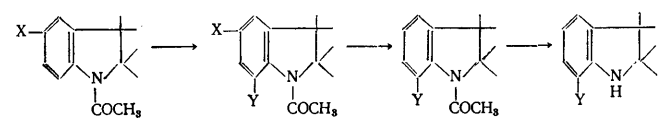
III. INTRODUCTION OF SUBSTITUENTS INTO THE BENZENE RING OF THE INDOLINE MOLECULE

The behaviour of indolines in electrophilic substitution reactions has been investigated with the aim of introducing substituents into the benzene ring of the indoline molecule. The question of the site of substitution in these reactions could not be solved by analogy between indoline (LXXXVIII) and *N*-methyl-*o*-toluidine (LXXXIX):



(LXXXVIII) (LXXXIX)

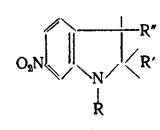
It has been established that these compounds and their *N*-acyl and *N*-alkyl derivatives behave in different ways in electrophilic substitution reactions[117]. The different behaviour of these systems was accounted for by the fact that in *NN*-disubstituted *o*-toluidine the CH_3 and NR_2 groups cannot lie in the plane of the benzene ring due to steric hindrance[117]. This leads to weakening of the conjugation between the NR_2 group and the benzene ring. In disubstituted *o*-toluidine electrophilic substitution takes place in the *para*-position with respect to the methyl group. As a result of the formation of the ring, the indoline molecule is coplanar and there is no weakening of the conjugation between the *p*-electrons of the nitrogen and the π-electrons of the benzene ring. Therefore electrophilic substitution takes place in the *para*-position with respect to the amino- (or acetamido-) group (i.e. position 5), since these groups have a more powerful directing effect. When reactions are carried out in a strongly acid medium, indoline is converted into the indolinium cation, as a result of which the substituents enter the *meta*-position with respect to the ammonium group, i.e. position 6. In the synthesis of 7-substituted indolines, position 5 is blocked by substituents which are readily eliminated and 1-acetylindoline is used as the starting material[118]:



The introduction of substituents into position 4 of the indoline ring, after protection of position 6, was not investigated.

1. Nitration, Nitrosation, and Azo-Coupling of Indolines

When indolines are nitrated with the nitrating mixture in sulphuric acid, the nitro-group enters into position 6. A number of 6-nitroindolines (XC) have been obtained in high yields[15,16,119-122]:

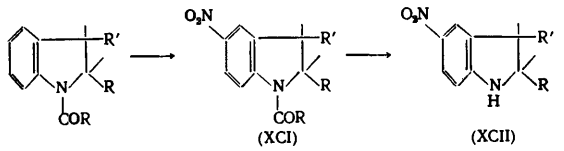


(XC)

R=R′=R″=H R=R′=H; R″=CH_3.
R=CH_3; R′=R″=H. R=C_2H_5; R′, R″=$(CH_2)_4$.
R=R″=H; R′=CH_3. R=R′=CH_3; R″=H.

A 6-nitro derivative of 2,3-dimethyl-1,7-trimethyleneindoline, which is in all probability a mixture of *cis*- and *trans*-isomers, has also been obtained[123,124]. The nitration of

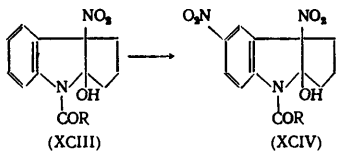
1-acylindolines gave a series of 1-acyl-5-nitroindolines (XCI), which were then converted into 5-nitroindolines (XCII)[16,44,45,119,125-127]:



(XCI) (XCII)

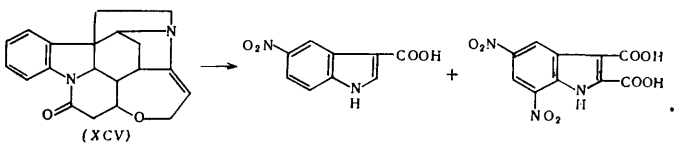
R=R'=H. R=CH_3; R'=H. R, R'=$(CH_2)_4$. R=H; R'=$(CH_2)_nCOOH$.

The nitration of *N*-acylindolines of complex structure (XCIII) has been described[128]:



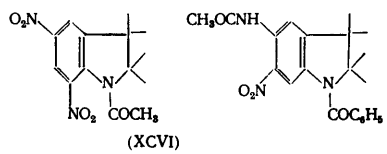
(XCIII) (XCIV)

Strychnine (XCV), which is a complex acylindoline, is nitrated in position 2 which corresponds to position 5 in the indole ring (oxidation and hydrolysis take place simultaneously)[129]:



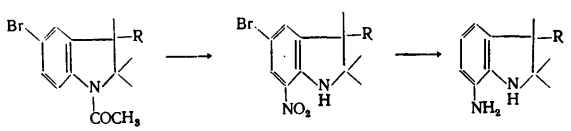
(XCV)

It is interesting to note that 5-nitro-derivatives are formed exclusively; the formation of 7-isomers has not been observed. However, after nitration of 1-acetylindoline, a certain amount of the 5,7-dinitro-derivative (XCVI) was isolated[119]. By further nitration of 1-acetyl-5-nitroindoline, the derivative was obtained in 42% yield[125]:



(XCVI) (XCVII)

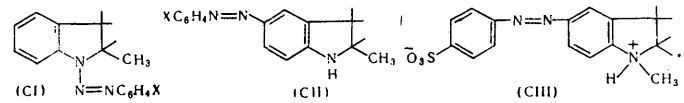
The nitration of 5-acetamido-1-benzoylindoline gave probably the 6-nitro-derivative (XCVII), while the product of the nitration of 1-benzoyl-6-diacetamidoindoline was probably the 4-nitro-derivative. The structure of the products obtained was not proved[16]. 5-Bromo-7-nitroindolines (XCIX), the key substances in the synthesis of 7-aminoindolines (C) and indoles, have been synthesised by the action of nitric acid on 1-acetyl-5-bromoindolines (XCVIII)[44,45,118,126,130]:



(XCVIII) (XCIX) (C)

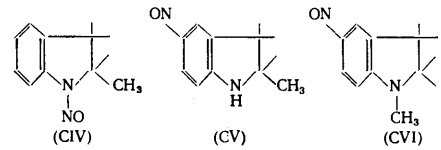
where R = H, CH_2COOH, and CH_2CH_2COOH.

In contrast to 2,3-dihydroindoles, the *N*-acetylated adduct of indole with sodium bisulphite (LVIII) forms on nitration a mixture of 5- and 7-derivatives, which on treatment with alkali yield a readily separated mixture of 5- and 7-nitroindoles[17,77]. On azo-coupling with phenyldiazonium salts in the presence of sodium acetate, 2-methylindoline forms diazoamino-compounds (CI); in a strongly acid medium the products are the diazo compounds (CII)[31]:



(CI) (CII) (CIII)

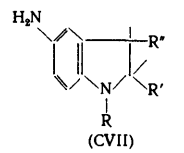
On coupling with diazotised sulphanilic acid, 1-methylindoline also forms the azo-dye (CIII). It proved possible to isolate the sodium salt of the dye from a strongly alkaline medium[131]. The nitrosation of indoline and 2-methylindoline yields *N*-nitroso-derivatives[30,122,132]. 2-Methyl-1-nitrosoindoline (CIV) undergoes the Fischer–Hepp rearrangement with formation of 2-methyl-5-nitrosoindoline (CV). 1-Methyl-5-nitrosoindoline (CVI) was obtained in the reaction between butyl nitrite and 1-methylindoline[122].



(CIV) (CV) (CVI)

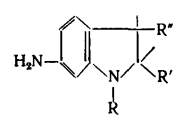
2. Aminoindolines

Aminoindolines have been investigated very thoroughly because, apart from their possible conversion into aminoindoles, they may serve as the starting materials for the preparation of alkoxy-, fluoro-, and other substituted indolines. Elimination of the nitro-group protecting position 5 or 6 also proceeds via the aminoindoline state. 5- and 6-aminoindolines, (CVII) and (CVIII) respectively, have been obtained by the reduction of the corresponding readily available nitroindolines[15,16,44,119,122,133-135]:



(CVII)

R=R'=R"=H;
R=R"=H; R'=CH_3;
R=COC_6H_5; R'=R"=H;
R=R'=H; R"=CH_2COOH.



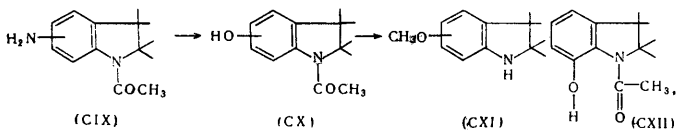
(CVIII)

R=R'=R"=H.
R=R'=H; R"=CH_3.
R=$COCH_3$; R'=R"=H.
R=R"=H; R'=CH_3.
R'=R"=H; R=CH_3.
R'=R"=H; R=COC_6H_5.

Hydrazine hydrate in the presence of Raney nickel[119] and also stannous chloride[15,133] have been used as the reducing agents. Nitroindolines have been hydrogenated over palladium on charcoal[134,135], over the Adams catalyst[16], and over Raney nickel[44]. Certain 5-aminoindolines have been obtained by the reduction of 5-nitroso- or 5-sulphophenylazo-derivatives[31,122]. This method of synthesis is particularly valuable for 5-amino-1-methylindoline, because a method of preparation of 1-methyl-5-nitroindoline has not been described[131]. When bromonitroindolines are

hydrogenated over palladium on charcoal, the bromine atom is eliminated and aminoindolines are produced. The method is suitable for the preparation of 7-aminoindolines.

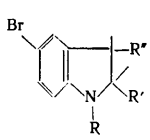
5-Bromo-1-methylindoline [131], 1-acetyl-7-iodoindoline[125], 1-acetyl-6-fluoroindoline [134], 1-acetyl-5-fluoroindoline [134], 1-acetyl-6-chloroindoline [134], and 1-acetyl-5-chloroindoline [134] have been obtained from the corresponding aminoindolines by the Sandmeyer reaction. The replacement of the amino-group by fluorine and chlorine takes place in high yields, the corresponding halogenoindolines being obtained on deacetylation. The conversion of 1-acetyl-5-amino-, 1-acetyl-6-amino-, and 1-acetyl-7-amino-indolines (CIX) into the corresponding hydroxy-derivatives (CX) (in yields of 77, 82, and 42% respectively) has been achieved [133,135]. 5-, 6-, and 7-methoxyindolines (CXI) have been obtained by the methylation of the hydroxy-group. The methylation yield is low in the case of 7-hydroxyindoline (CXII); the authors attribute this to the presence of a hydrogen bond in this compound [135].



(CIX) (CX) (CXI) (CXII)

3. Halogenation of Indolines

5-Bromo-derivatives (CXIII) are formed when indolines are brominated in acetic acid or in the bromination of 1-acetylindolines [44,45,118,119,126,127,131,136,137].

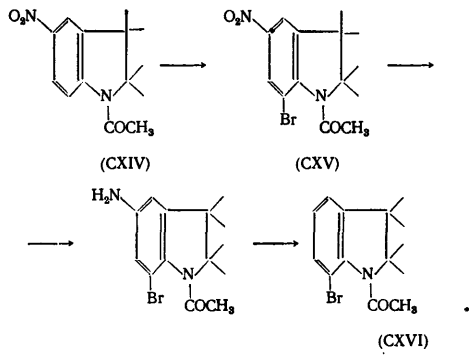


(CXIII)

R=R′=R″=H. R=COC$_6$H$_5$; R′=H; R″=CH$_2$COOH.
R=R″=H; R′=CH$_3$. R=H; R′, R″=(CH$_2$)$_4$.
R=CH$_3$; R′=R″=H. R=H; R′R″=(CH$_2$)$_3$.
R=H; R′=R″=CH$_3$.

The non-protonated indoline species appear to react in the bromination of indolines in a mixture of sulphuric and acetic acids. 6-Bromo-2,3-dimethylindoline has been obtained by the bromination of 2,3-dimethylindoline in a strongly acid medium [137]. The paper describing the synthesis was the first communication about the possibility of a direct synthesis of 6-bromoindolines. It was not stated whether the 5- and 6-bromo-2,3-dimethylindolines were pure substances or mixtures of *cis*- and *trans*-forms [137].

The bromination of the sodium salt of 1-acetylindoline-2-sulphonic acid (LVIII) followed by treatment with alkali gave 5-bromoindole in 70% yield [17,77]. When ICl is allowed to act on compound (LVIII), the 5-iodo-derivative is produced and from the latter 5-iodoindole can be obtained by the action of alkali [17,77]. 5-Iodoindoline has been obtained by the action of ICl on 1-acetylindoline with subsequent hydrolysis of the acetyl group [138]. The attempt to prepare 5-chloroindole by the action of chlorine on the adduct of indole and sodium bisulphite (LVIII) was unsuccessful [17,77]. Chloro- and fluoro-indolines have been obtained, as stated above, from the corresponding 1-acetamidoindolines [134]. The attempt to prepare fluoroindolines from bromoindolines was unsuccessful [134]. The 7-bromo-derivative (CXV) has been obtained by the bromination of 1-acetyl-5-nitroindoline (CXIV). The reduction of the nitro-group and the elimination of the amino-group gave 1-acetyl-7-bromoindoline (CXVI) [126]:

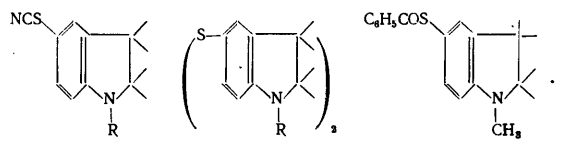


(CXIV) (CXV) (CXVI)

There are data indicating high physiological activity of 1-acyl-5-halogenoindolines [139].

4. Thiocyanato- and Mercapto-Derivatives of Indoline

5-Mercapto-derivatives of indoles and indolines, the thio-analogues of hydroxyindole derivatives which exhibit high pharmacological activity, have been investigated very little so far. 5-Thiocyanato-derivatives (CXVII), which are both of intrinsic interest and are important as key substances for the synthesis of 5-mercaptoindoline or 5-mercaptoindole derivatives, have been obtained by the thiocyanation of indoline derivatives [140]:

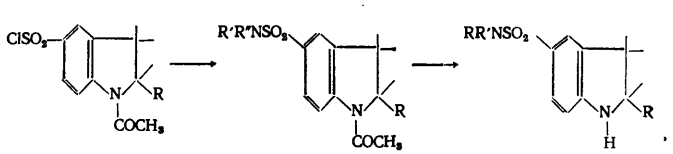


(CXVII, R=H, CH$_3$) (CXVIII, R=H, CH$_3$) (CXIX)

The treatment of 5-thiocyanatoindolines (CXVII) with alkali gave the corresponding disulphides (CXVIII) and the reduction of 1-methyl-5-thiocyanatoindoline with tin in hydrochloric acid led to 5-mercapto-1-methylindoline, which was isolated as the *S*-benzoyl derivative (CXIX) [140].

5. Chlorosulphonation of Indolines and Sulphonamides of the Indoline Series

By the chlorosulphonation of 1-acetylindoline, 1-acetylindoline-5-sulphonyl chlorides (CXX) were obtained, from which a number of indoline-5-sulphonamides (CXXI) [117,138, 141-143] and indoline-5-sulphonic acids were synthesised [117]:



(CXX) (CXXI, R=H, CH$_3$)

As stated above, indoline-6-sulphonamides (LXII) have been obtained by the cyclisation of the indoline ring. The sulphoureides (CXXII) and (CXXIII) have been prepared

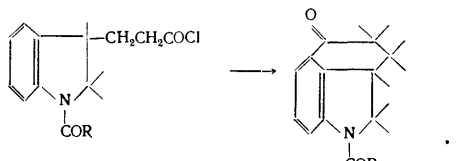
from indoline-5-sulphonamides and indoline-6-sulphonamides [141,143]:



(CXXII) (CXXIII)

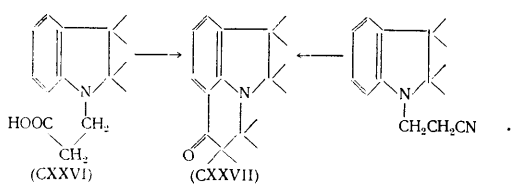
6. Acylation and Alkylation of Indolines

Intramolecular *C*-acylation of derivatives of indolinealkanoic acids has been investigated in connection with studies on the synthesis of indole alkaloids. The first stage in the synthesis of lysergic acid consists in the conversion of 1-acylindoline-3-propionic acid into the acid chloride (CXXIV) which is cyclised under the conditions of the Friedel–Crafts reaction with the formation of the corresponding tricyclic derivative [14,144,145] (CXXV):



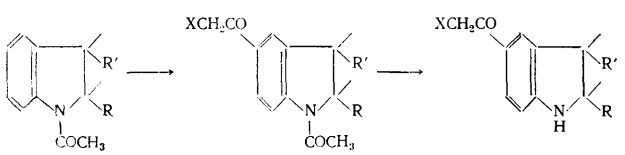
(CXXIV) (CXXV)

The intramolecular cyclisation of indoline-1-propionic acid (CXXVI) by heating with perfluoroacetic anhydride led to the corresponding tricyclic ketone (CXXVII) [146]. The same oxo-derivative (CXXVII) was obtained from *N*-(β-cyanoethyl)indoline (CXXVIII) [147]:



(CXXVI) (CXXVII)

The syntheses of alkyl *C*-indolyl ketones and especially methyl 5-indolyl ketone has been attracting attention in recent years in connection with the discovery of the pharmacological activity of 5-acetyltryptamine and its derivatives [148]. A series of 5-acetyl- and 5-chloroacetyl-indolines (CXXIX) have been obtained by the Friedel–Crafts acylation of 1-acetylindolines [149,150]:

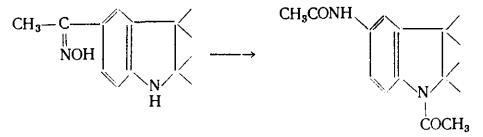


(CXXIX)

R=R′=H; X=H.
R=R′=H; X=Cl.
R=CH$_3$; R″=X=H.
R=CH$_3$; X=Cl; R′=H.
R, R′=(CH$_2$)$_4$; X=H.

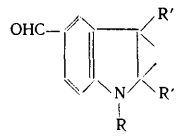
The acylation yields mainly the 5-derivative, but in the chloroacetylation of 1-acetylindoline 3% of a product, which was probably 1-acetyl-7-chloroacetylindoline, was isolated in addition to 83% of the 5-chloroacetyl derivative [149].

Acetamidoindolines have been obtained from the oximes of indolinyl ketones by the Beckmann reaction [149]. For example:



Clemmensen reduction of 5-acetyl- and 5-chloroacetylindolines gives 5-ethylindolines [149].

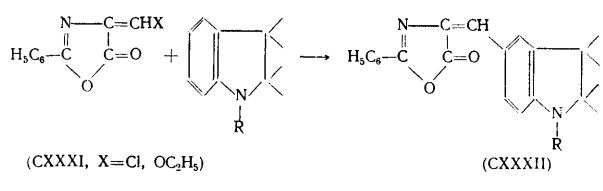
The Vilsmeier reaction has been used to prepare indoline-5-aldehydes. Indoline-5- and indole-5-aldehydes are of interest as key substances in the synthesis of various 5-analogues of tryptamine and tryptophan. A series of 1-alkyl-5-formylindolines (CXXX) have been obtained by the formylation of *N*-alkylindolines with methylformanilide and phosphorus oxychloride [151]:



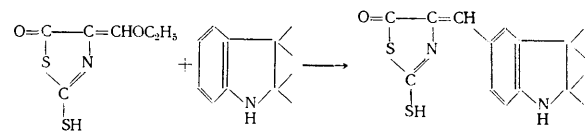
R=n-C$_4$H$_9$; R′=CH$_3$; R″=H. R=CH$_2$CH$_2$CN; R′=CH$_3$; R″=H.
R=R′=CH$_3$; R″=H. R=CH$_2$C$_6$H$_5$; R′=C$_6$H$_5$; R″=H.
R=C$_2$H$_5$; R′=CR$_3$; R″=H. R=H; R′R″=(CH$_2$)$_4$.

(CXXX)

The formylation of indoline and 1-methylindoline with dimethylformamide gives the corresponding 5-formyl derivatives (CXXX, R = R″ = H, R = H or CH$_3$) [152,153]. 1-Methylindoline yields also a certain amount of the 5,7-diformyl derivative [153]. The antitubercular activity of the thiosemicarbazone of 1-methylindoline-5-aldehyde has been described [154]. When phosphorus oxychloride or phosgene are allowed to act on 1-formylindolines, the latter are converted into 5-formylindolines. The authors call this reaction the migration of the formyl group to position 5, although it can be supposed that intermolecular formylation actually takes place. A number of aldehydes [CXXX, R = R″ = H, R′ = CH$_3$; R = R″ = H, R′ = C$_6$H$_5$; R = H and R′, R″ = (CH$_2$)$_4$] have been obtained by this method [155]. 4-(Indolin-5′-ylmethylene)-2-phenyl-5-oxazolone (CXXXII) has been obtained in the reaction of chloro- or ethoxy-methylene-2-phenyl-5-oxazolone (CXXXI) while the reaction of indoline with 4-ethoxymethylene-2-mercapto-1,3-thiazol-5-one (CXXXIII) gave the corresponding derivative of indoline and thiazolone (CXXXIV) [152]:



(CXXXI, X=Cl, OC$_2$H$_5$) (CXXXII)

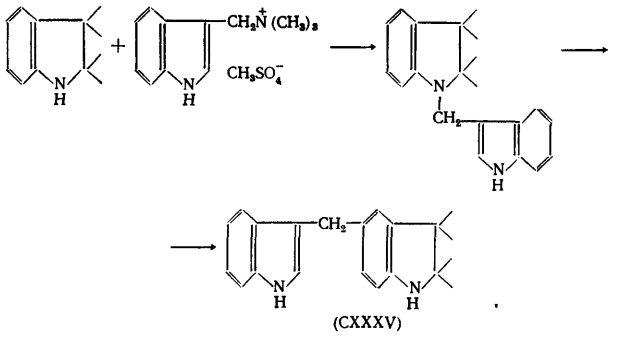


(CXXXIII) (CXXXIV)

Similar *C*-substitution of indoline takes place with high yield on heating in a neutral medium. Indolinylmethylenephenylazlactone (CXXXII, R = H) has been used as the starting material for the synthesis of 5-isotryptophan (5-indolylalanine) [152].

The *C*-alkylation of indolines has been almost not investigated. It has been shown that the reaction of the

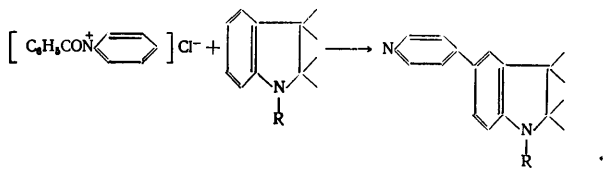
quaternary salt of gramine with indoline yields 5-scatylindoline (CXXXV)[156,157]:



(CXXXV)

Indoline can probably be alkylated also by other ammonium derivatives.

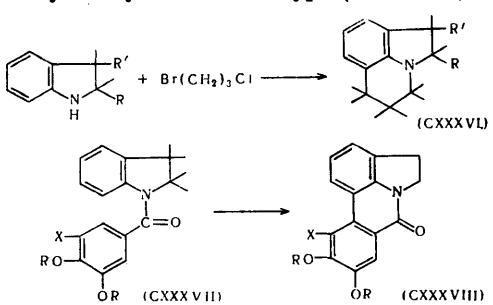
The reaction of 1-alkylindolines with 1-acylpyridinium salts in the presence of Lewis acids leads to 1-alkyl-5-(pyrid-4′-yl)indolines. 1-Alkyl-5-benzoylindolines are formed as side-products[158]:



1-Acylquinolinium salts react with 1-alkylindolines without catalysts with formation of 1-alkyl-5-(1′-benzoyl-1′,2′-dihydroquinolin-2′-yl)indolines, which are converted by alkaline hydrolysis into 1-alkyl-5-(quinolin-2′-yl)indolines[159].

7. Synthesis of Tricyclic Systems Based on Indolines

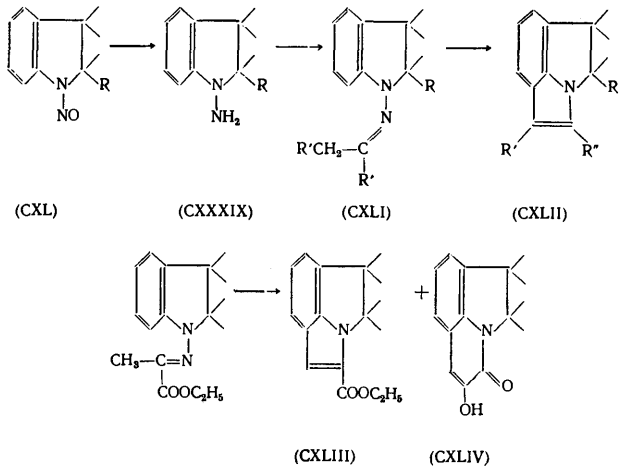
In connection with studies on the structure of indole alkaloids, the possibility of synthesising condensed indole and indoline systems has been investigated. When 1-bromo-3-chloropropane was allowed to react with indoline, lilolidine and its derivatives (CXXXVI) were obtained[160]. Similarly 9,10-dimethyl-lilolidine (CXXXVI, R = R′ = CH_3) is formed from 2,3-dimethylindoline[161]. It is not clear whether the authors dealt with pure substances or with mixtures of *cis*- and *trans*-isomers. The decomposition of diazotised derivatives of *o*-aminobenzoylindoline (CXXXVII) under the conditions of the Pschorr reaction leads to tricyclic systems of the type (CXXXVIII)[118,162]:



(CXXXVI) (CXXXVII) (CXXXVIII)

A similar cyclic system could not be obtained from 7-amino-1-benzoylindoline. The cyclisation can only be achieved in the presence of several alkoxy-groups in the benzene residue.

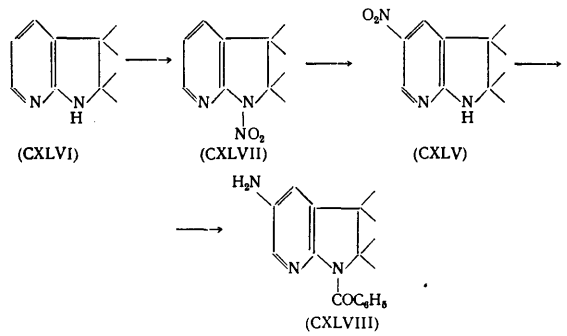
The use of indoline derivatives for the synthesis of cyclic systems by the Fischer reaction has also been described. 1-Aminoindolines (CXXXIX), prepared by the reduction of 1-nitrosoindolines (CXL), form with carbonyl compounds the hydrazones (CXLI), from which the tricyclic indole derivatives (CXLII), (CXLIII), and (CXLIV) were obtained[163-166]:



(CXL) (CXXXIX) (CXLI) (CXLII) (CXLIII) (CXLIV)

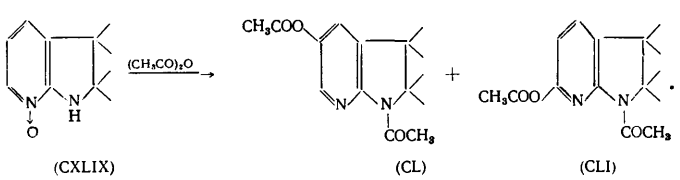
8. Substitution Reactions of Azaindolines

The substitution reactions in the series of pyridinopyrrolines (7-azaindolines) have been investigated with the aim of synthesising 7-azaindole derivatives[167]. 5-Nitro-7-azaindoline (CXLV) has been obtained by the nitration of 7-azaindoline (CXLVI). 1-Nitro-7-azaindoline (CXLVII) forms as an intermediate. 5-Amino-1-benzoyl-7-azaindoline (CXLVIII) has been prepared[167]:



(CXLVI) (CXLVII) (CXLV) (CXLVIII)

By allowing peracetic acid to react with 7-azaindoline, the corresponding *N*-oxide (CXLIX) was obtained and under the action of acetic anhydride the oxide was converted into a readily separated mixture of 5-acetoxy-1-acetyl-7-azaindoline (CL) and 6-acetoxy-1-acetyl-7-azaindoline (CLI). On hydrolysis, these compounds gave 5- and 6-hydroxy-7-azaindolines:



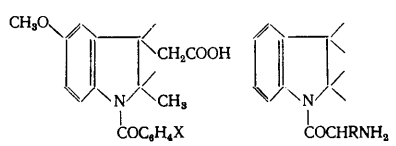
(CXLIX) (CL) (CLI)

It has been shown that 4-methyl-7-azaindoline derivatives are capable of forming 4-styryl derivatives [105]. The halogen in halogeno-7-azaindolines has been replaced by a methoxy-group and iodine [105]. The conditions of the dehalogenation of 6-chloro-7-azaindoline, 2,4-dichloro-7-azaindoline, and 4,6-dichloro-5-azaindoline have been investigated [113].

IV. INTRODUCTION OF SUBSTITUENTS INTO THE PYRROLE RING OF THE INDOLINE MOLECULE

The capacity of indolines to form *N*-derivatives, a property characteristic of all aromatic amines, was used to produce *N*-acyl- and *N*-alkyl-indoles, *N*-glycosylindoles, and also a quaternary indole salt, dimethylindolium perchlorate, which are difficult to obtain.

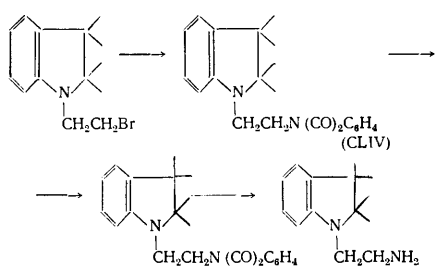
1-Acylindolines. When acted upon by acylating agents, indoline, sodium indoline-2-sulphonate, and 3-hydroxy-indoline form *N*-acyl derivatives. An enormous number of a wide variety of indoline derivatives, obtained by the action of acid anhydrides, arenesulphonyl chlorides, diketen [139], etc., have been described. We shall examine only those *N*-acylindolines which have been converted into the corresponding indole derivatives. In recent years much work has been done on the study of 1-benzoylindoline-3-alkanoic acids [for example, compound (CLII)]. These compounds have been converted into indomethacin (XV) and its analogues. The Merck Co. has published a number of patents dealing with the synthesis of compounds of this type [46,47]:



(CLII) (CLIII)

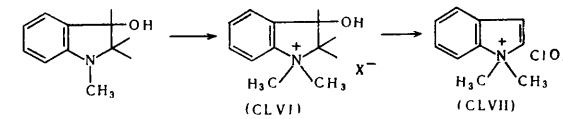
N-Aminoacyl derivatives of indoline (CLIII) have been investigated with the aim of converting them into the amino-acid derivatives of indole [168]. The principal difficulties arising in the preparation of *N*-acylindoles from *N*-acylindolines are encountered in the dehydrogenation stage. Probably the study of the *N*-acylation of the readily dehydrated 3-hydroxyindoline derivatives would prove very useful.

1-Alkylindolines and quaternary indolinium salts. *N*-alkylation of indolines and 3-hydroxyindolines has been investigated in great detail. Particular attention has been devoted to the preparation of derivatives of 1-(β-aminoethyl)indolines (CLIV), used for the synthesis of 1-isotryptamines (CLV) [169-172]:



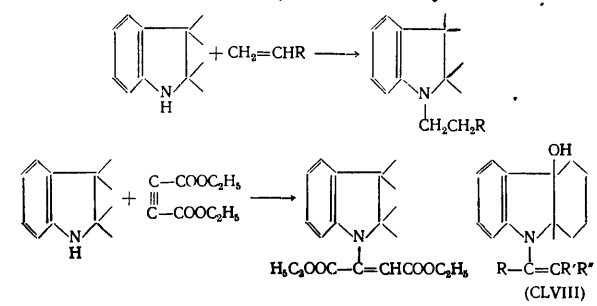
(CLV)

The quaternary 3-hydroxyindolinium salt (CLVI) has served as the starting material for the preparation of the quaternary indolium salt (CLVII) [18]:



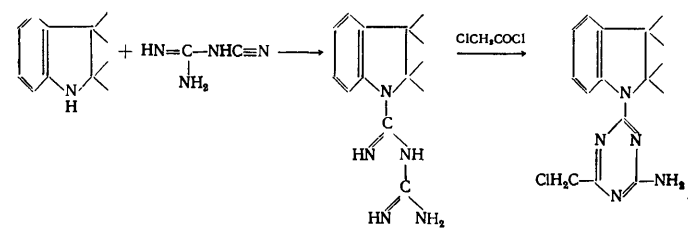
(CLVI) (CLVII)

Like other aromatic amines, indoline is capable of adding to the activated double bond of acrylonitrile [146,173], vinylpyridines [174], and also acetylenedicarboxylic acids [175]:

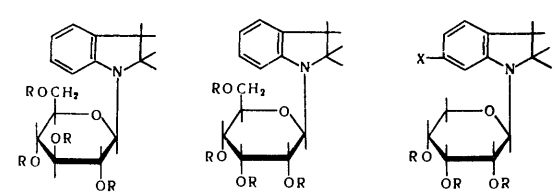


(CLVIII)

However, in the conversion to indole derivatives difficulties are encountered in this case in the dehydrogenation stage. When the corresponding hydroxyindoline derivative (CLVIII) is used, the conversion into indoles presents no difficulties [175]. The addition of indoline to the −C≡N bond has been described [176]:



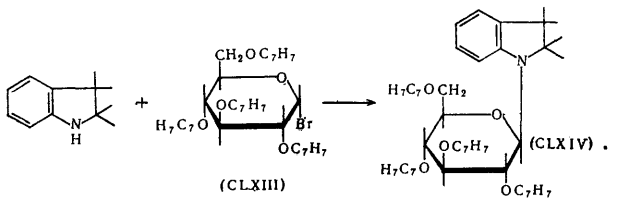
1-Glycosylindolines. In connection with the discovery of the antiviral activity of nucleoside and nucleotide analogues, the study of the properties of 1-glycosylindoles is of great interest. The investigations have acquired special importance after the discovery of the antibiotics tubercidin and toyokamycin. 1-Glycosylindolines have been used as the starting materials for the synthesis of 1-glycosylindoles [177-182]. 1-Glycosylindolines belong to the class of arylaminoglycosides, which have been little investigated. They are formed when indoline reacts with a hexose or pentose. 1-(D-β-Glucopyranosyl)indoline (CLIX, R = H) [177,178], 1-(D-β-galactopyranosyl)indoline (CLX, R = H) [179], 1(D-β-ribopyranosyl)indoline (CLXI, R = H) [180], 1-(D-β-ribopyranosyl)-6-nitroindoline (CLXII, R = H) [181], and their *O*-acetyl derivatives (CLIX, CLX, CLXI, CLXII, R = $COCH_3$) have been obtained.



(CLIX) (CLX)

(CLXI, X = H); (CLXII, X = NO_2).

The pyranoside structure of the products obtained has been confirmed by the fact that they have also been isolated in the reaction between *O*-acetylated pyranosyl acetates or acetohalogenopyranoses and indoline. Furthermore, in the hydrolysis of *O*-acetylated glycosylindolines it proved possible to isolate the corresponding *O*-acetylated pyranoses. The conclusion that 1-glycosylindolines and their derivatives have the β-configuration is based on the analysis of the molecular rotation and the infrared spectra. The formation of α-anomers could not be observed. Tetra-*O*-benzylglucopyranosyl bromide (CLXIII) has also been allowed to react with indoline, the tetra-*O*-benzyl derivative of glucopyranosylindoline (CLXIV) being obtained[182]:



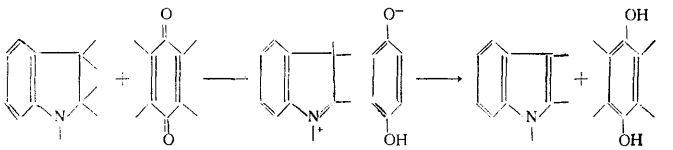
(CLXIII) (CLXIV).

V. CONVERSION OF INDOLINE DERIVATIVES INTO INDOLES

1. Dehydrogenation of Indolines

A wide variety of dehydrogenating agents are used to convert indolines into indoles—quinones with high oxidation potentials (chloranil, 2,3-dichloro-4,5-dicyano-*p*-benzoquinone), the pyridine complex of $CuCl_2$, $Hg(OCOCH_3)_2$, NiO_2, MnO_2, and others. The oxidation of indolines with atmospheric oxygen under various conditions and also catalytic dehydrogenation in the presence of Raney nickel, the Adams catalyst, palladium black or palladium on charcoal, nickel chromite, and other catalysts has also been described. The specific properties of the indole ring preclude the use of dehydrogenating agents such as sulphur and selenium, since indoles react with these substances[183].

The mechanism of the effect of quinones and other dehydrogenating agents on indoline has not been investigated. However, on the basis of general hypotheses[184], one can assume that at the beginning of the dehydrogenation process a hydride ion is removed, this being facilitated by the high-electron-donor capacity of the >NR group. The transition complex (CLXV) thus produced is then converted into indole and hydroquinone.



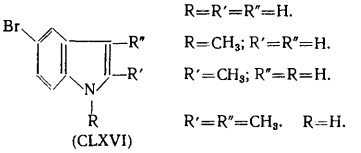
(CLXV)

It can be assumed that in other cases too, for example in heterogeneous catalysis, the initial dehydrogenation step is the removal of a hydride ion and the overall dehydrogenation mechanism is as follows:

$$\text{indoline} + A \rightleftharpoons \text{indole}.\ H^+.AH^- \rightarrow \text{indole} + AH_2,$$

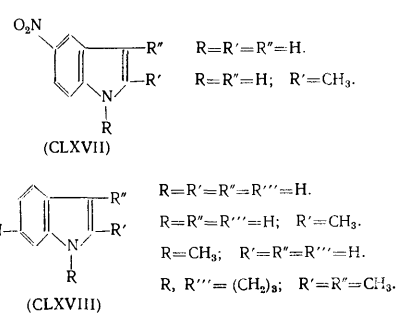
A being the dehydrogenating agent. In the dehydrogenation with chloranil and in catalytic dehydrogenation electron-donor substituents, which favour the removal of a hydride ion, also facilitate the dehydrogenation. In the dehydrogenation with quinones the *trans*-configuration of the hydrogen ion eliminated is not obligatory, since *cis*-2,3-dimethylindoline forms 2,3-dimethylindole in 38% yield[93], which is consistent with the proposed mechanism of dehydrogenation by quinones. In dehydrogenation with palladium on charcoal selective *trans*-dehydrogenation is also not observed[25].

The most widely used dehydrogenating agent is chloranil. Dichlorodicyanoquinone, which has a higher redox potential, is finding increasing application in organic synthesis. Yet another property makes it a valuable dehydrogenating agent—dichlorodicyanohydroquinone formed in the reaction is sparingly soluble in benzene and xylene, which facilitates the isolation of the reaction products. As already mentioned, chloranil has been used to dehydrogenate 2,3-dimethylindoline[93], unsubstituted indoline and other alkylindolines[40], and also 5-ethoxy-1-methylindoline[35]. This agent has been used in the dehydrogenation of halogenoindolines. The following 5-bromoindoles (CLXVI) have been obtained[119,121,127]:



(CLXVI)

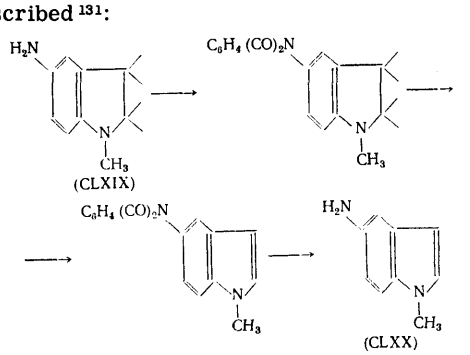
6-Bromo-2,3-dimethylindole has also been prepared[137]. The dehydrogenation of 5-iodoindoline[138], 5- and 6-chloroindolines, and fluoroindolines[134] has been described. A number of nitroindoles (CLXVII and CLXVIII) have been synthesised by boiling with chloranil in xylene[15,119,123,124]:



(CLXVII) (CLXVIII)

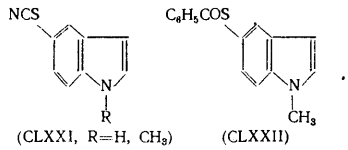
When a second nitro-group is introduced into the indoline molecule, the redox potential of chloranil proves insufficient and dinitroindoline cannot be dehydrogenated by boiling with chloranil in xylene[125].

In the dehydrogenation of aminoindolines with quinones it is necessary to protect the amino-group in order to avoid its undesirable interaction with chloranil. The following method for the conversion of 5-amino-1-methylindoline (CLXIX) into the corresponding indole (CLXX) has been described[131]:



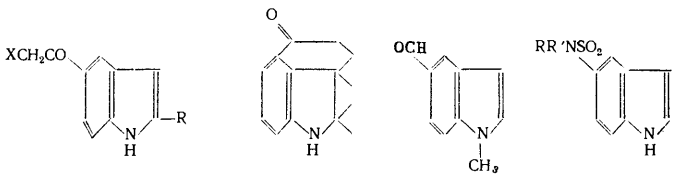
(CLXIX) (CLXX)

5-Thiocyanatoindoles (CLXXI) have been obtained by boiling 5-thiocyanatoindolines with chloranil in xylene. 5-Benzoylmercapto-1-methylindole (CLXXII) has been obtained similarly [140]:



(CLXXI, R=H, CH_3) (CLXXII)

The 5,5′-disulphide of 1-methylindole has been described [140]. Indoles containing an acyl group in the benzene ring have also been synthesised by dehydrogenating the corresponding indolines with chloranil. Chloranil has been used in the synthesis of the ketones (CLXXIII) [149]:

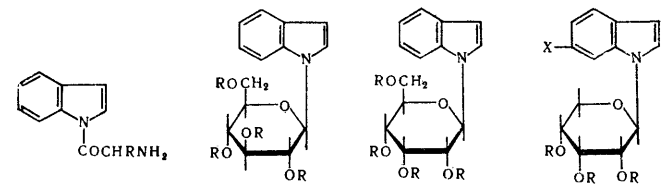


(CLXXIII, R=H; X=H·R=CH_3; X=H. R=H; X=Cl·R=CH_3; X=Cl) (CLXXIV) (CLXXV) (CLXXVI)

Heat is used in the dehydrogenation with quinones. At room temperature the ketone (CLXXIV) could not be dehydrogenated with chloranil and dichlorodicyanoquinone gave the corresponding indole in 5% yield only [185]. In contrast to 4-(indolin-5′-yl)methylene-5-oxo-2-phenyloxazole (CXXXII, R = H), 1-methylindoline-5-aldehyde was converted into 1-methylindole-5-aldehyde (CLXXV) on boiling with chloranil in xylene. The dehydrogenation of indoline-5-sulphonamides yielded a series of indole-5-sulphonamides (CLXXVI) [117,138,141]. Convenient solvents for the dehydrogenation of indolinesulphonamides and other indoline derivatives which are sparingly soluble in xylene are 1,2-dimethoxyethane [141], diglyme, and dimethylformamide [181].

The reaction with chloranil or dichlorodicyanoquinone also constitutes a general method for the dehydrogenation of 1-alkyl(aryl)-7-azaindolines [103,105,106]. A large number of 7-azaindole derivatives have been obtained. As with indolines, the introduction of electron-acceptor substituents into the azaindoline molecule hinders dehydrogenation, while electron-donor substituents facilitate it [111]. It is noteworthy that, as a result of the lower electron density of the pyridine ring compared with the benzene ring, azaindolines are dehydrogenated under more severe conditions than indolines. In their capacity for dehydrogenation azaindolines are similar to nitroindolines. *N*-Acylation of indolines also hinders dehydrogenation, since the electron density of the pyrrole ring is thereby reduced. However, it has proved possible to obtain a number of *N*-acylindoles from the corresponding indolines. *N*-Aminoacyl derivatives of indole (CLXXVII) have been synthesised from the *N*-aminoacyl derivatives of indoline (CLIII) by boiling with chloranil in xylene [168]. The last stage in the synthesis of indomethacin (XV) consists in the dehydrogenation with chloranil of 1-(*p*-chlorobenzoyl)-2,3-dehydro-5-methoxy-2-methylindole-3-acetic acid (CLII) [47]. Probably the presence of the methoxy-group in position 5 facilitates the dehydrogenation despite the opposed effect of the *p*-chlorobenzoyl residue. 1-Acetyl-5-bromoindoline-3-acetic and 1-acetyl-5-nitroindoline-3-acetic acids could not be dehydrogenated with chloranil [44].

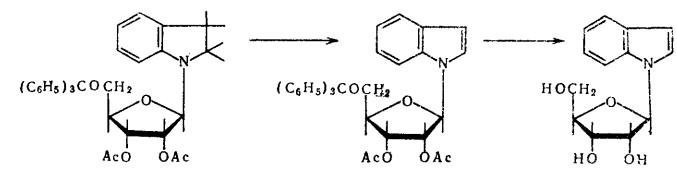
The dehydrogenation of *N*-glycosylindolines has been investigated in detail. The dehydrogenation of 1-(D-β-tetra-*O*-acetylglucopyranosyl)indoline (CLIX, R = $COCH_3$) by boiling with chloranil in xylene gives the corresponding indole in 32% yield (CLXXVIII, R = $COCH_3$) [177,178]. When dichlorodicyanoquinone is used in the synthesis, the yield is quantitative [182]. Dichlorodicyanoquinone has also been used to synthesise 1-(D-β-tetra-*O*-benzylglucopyranosyl)-indole (CLXXVIII, R = $CH_2C_6H_5$) [182].



(CLXXVII) (CLXXVIII) (CLXXIX) (CLXXX)

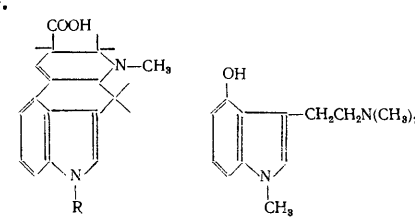
This reagent has also been employed in the synthesis of 1-(D-β-tetra-*O*-acetylgalactopyranosyl)indole (CLXXIX, R = $COCH_3$) [179] and 1-(D-β-tri-*O*-acetylribopyranosyl)indole (CLXXX, X = H, R = $COCH_3$) [180]. In the dehydrogenation of 6-nitro-1-(D-β-tri-*O*-acetylribopyranosyl)indoline (CLXII, R = $COCH_3$) even boiling with chloranil in xylene is insufficient to complete the reaction. The reaction mixture consists of the indoline (CLXII, R = $COCH_3$) and the indole (CLXXX, X = NO_2, R = $COCH_3$), which can be separated after deacetylation. The yield of indole (CLXXX, X = NO_2, R = H) is 19%. [181]

Dichlorodicyanoquinone has been used as the dehydrogenating agent in the conversion of 1-(D-β-5′-*O*-trityl-2′,3′-di-*O*-acetylribofuranosyl)indoline into the corresponding indole derivative which is a key substance in the synthesis of 1-(D-β-ribofuranosyl)indole, an indole analogue of nucleosides [186]:



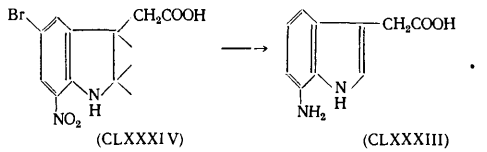
9,10-Phenanthroquinone has also been used as a dehydrogenating agent for indolines [185].

The catalytic dehydrogenation of indoline derivatives has been extensively studied. There is great scope for synthesis using Raney nickel as the catalyst. In the conversion of dehydrolysergic acid (XXXVIII, R = H) into lysergic acid (CLXXXI, R = H) the former was boiled in water with Raney nickel and sodium arsenate [14]. In contrast to this catalyst, which aromatises the pyrrole ring, the use of palladium on charcoal leads to the aromatisation of the naphthalene ring. 4-Hydroxy-3-(β-dimethylaminoethyl)-1-methylindole (CLXXXII) has been obtained by the dehydrogenation of the corresponding indoline over Raney nickel in water [91].



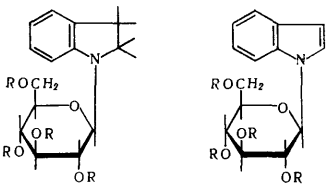
(CLXXXI) (CLXXXII)

In those cases where the indoline molecule contains a group capable of being reduced, Raney nickel causes simultaneous dehydrogenation of the pyrroline ring and reduction of this group. Thus on being boiled with Raney nickel or with the Raney alloy, nitroindolines are converted into aminoindoles. 5- and 6-Aminoindoles, 5-aminoindole-3-acetic acid and 5-aminoidnole-3-propionic acid have been obtained by this method[44,45]. In the presence of a halogen in the indoline molecule, dehydrogenation is accompanied by the elimination of the halogen. By boiling bromonitroindoline with Raney nickel, 7-aminoindole and 7-aminoindole-3-acetic acid (CLXXXIII) have been obtained in one stage from 1-acetyl-5-bromo-7-nitroindoline and 5-bromo-7-nitroindole-3-acetic acid (CLXXXIV) respectively[44,45]:



(CLXXXIV) (CLXXXIII)

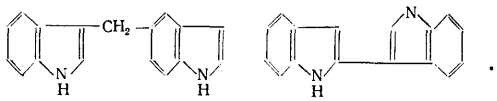
It is interesting that, using Raney nickel, it is difficult to reduce the substituent without the simultaneous dehydrogenation of the pyrroline ring. Thus neither aminoindoline nor nitroindole can be obtained from nitroindoline in the presence of Raney nickel. The nitro-group is reduced even when the reaction is carried out in nitrobenzene or in the presence of added maleic acid. The same phenomenon has been observed in the dehydrogenation of 1-(D-β-tetra-*O*-benzylglucopyranosyl)indoline (CLXXXV, R = $CH_2C_6H_5$)[181]. Dehydrogenation and debenzylation take place simultaneously. The indole (CLXXXVI, R = H) forms in 39% yield. Chromatographic analysis of the reaction mixture showed the absence of the corresponding debenzylated glucosylindoline (CLXXXV, R = H).



(CLXXXV) (CLXXXVI)

Even hydrogenation of compound (CLXXXV, R = $CH_2C_6H_5$) over Raney nickel at 50°C and 50 atm is accompanied by the formation of the indole derivative (CLXXXVI, R = H). In contrast to the *O*-benzyl derivative, the acetylated glucopyranosylindoline (CLXXXV, R = $COCH_3$) and also the unprotected glucopyranosylindoline (CLXXXV, R = H) are not completely dehydrogenated on boiling with Raney nickel. Thus the presence in the molecule of a reducible group greatly facilitates the dehydrogenation. Probably intramolecular transfer of a hydride ion to the reducible group takes place very readily in the complex indole.H^+.AH^- formed in the heterogeneous catalytic dehydrogenation.

Palladium black and palladium on charcoal are also widely used in the dehydrogenation. Hydrogen acceptors—nitrobenzene, cinnamic acid, and maleic anhydride—are frequently added in such reactions. Thus indoline has been converted into indole by heating with palladium black and cinnamic acid[57]. 5- and 6-nitroindoles[16], 6-benzamido-1-methylindole[15], 1-methyl-6-phthalimidoindole[15], and a series of indole-5-sulphonamides (CLXXXVI)[42] have been obtained under the same conditions:

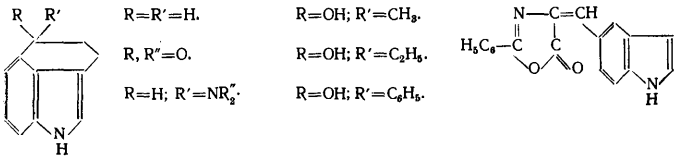


(CLXXXVII) (CLXXXVIII)

The dehydrogenation of indoline derivatives in the presence of catalysts without using hydrogen acceptors has also been described. The following products have been obtained: 5-scatylindole (CLXXXVII)[156] from 5-scatylindoline (CXXXV)[156], 2,3′-di-indolyl (CLXXXVIII) from the indole dimer (LIX)[79], 5-, 6-, and 7-methoxyindoles from the corresponding methoxyindolines[135], and the ketone (CLXXXIX, R, R′ = O) from the ketone (CLXXIV)[184]. 5-Aminoindoline has been converted into 5-aminoindole by heating with palladium on charcoal in the absence of solvent at 190°C.[44] Alkylindolines have also been dehydrogenated by heating with palladium on charcoal up to 200°C.[25] 4-(Indolin-5′-yl)methylene-5-oxo-2-phenyloxazole (CXXXII, R = H), which could not be dehydrogenated with chloranil, gave the corresponding indole derivative (CXC) after boiling for two days with palladium black in xylene[152]. 5,7-Dinitroindoline could not be converted into dinitroindole by boiling with palladium black in mesitylene[125]. The attempt to dehydrogenate 1,1-dimethylindolinium chloride by boiling with palladium black in xylene did not yield the corresponding quaternary indolium salt[18].

The dehydrogenation of indoline on the $Ni/NiCrO_2$ catalyst at 200°C has been described[187]. The pyridine complex of $CuCl_2$ has also been used as the oxidising agent for indolines[91,142]. The yields of indole and 1-methylindole when the corresponding indolines were heated with cupric chloride in pyridine were 55–60%.[142] Similarly a number of 4- and 6-methoxyindolines have been converted into the corresponding indoles[91]. So far, it has not proved possible to use this reagent in the synthesis of indoles containing electron-acceptor groups.

Oxidation with manganese dioxide in benzene[188] or methylene chloride[185] has also been described. The yield of indoline was 56–59%. The following compounds (CLXXXIX) have been obtained by shaking the corresponding indolines with manganese dioxide in methylene chloride[185]:



(CLXXXIX) (CXC)

Indole-3-propionic acid has also been synthesised by the oxidation of indoline-3-propionic acid[185]. 2-Methylindoline, 2,3-dimethylindoline, and 1-acyl derivatives of indoline could not be dehydrogenated by this method[185]. Attempts have been made to oxidise indolines with nickel peroxide[185]. The dehydrogenation of 2- and 3-methylindolines by distillation from silver sulphate has been described[189].

The classical dehydrogenating agent $Hg(OCOCH_3)_2$ is relatively unsuitable for the indoline series, since indole compounds are mercurated by mercury salts, probably with formation of 1,3-dimercuri-derivatives[190]. However, in

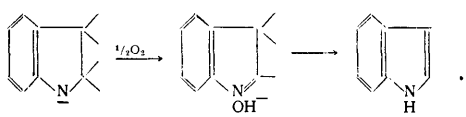
some cases dehydrogenation has been achieved. The dehydrogenation of dihydrolysergic acid derivatives (XXXVIII) with $Hg(OCOCH_3)_2$ has been described[57].

Dinitroindolines can be oxidised to indoles with nitric acid, the oxidation being accompanied by the nitration of the pyrrole ring of indole. 3,5,7-Trinitroindole has been obtained from 5,7-dinitroindoline[125] and 5-nitro and 5,7-dinitroindolecarboxylic acid (XCV) (see p. 756) have been obtained from strychnine.

When 2-methylindoline was heated with concentrated hydrochloric acid at 240°C, 2-methylindole was formed in 28% yield[25]. The mechanism of the process has not been established. Probably atmospheric oxygen is involved. Very interesting data have been obtained on dehydrogenation with atmospheric oxygen in the study of the sodium salts of indolines and azaindolines[22,113]. It has been found that the formation of the *N*-sodio-derivative of indoline in liquid ammonia, toluene, or other solvents is accompanied by the oxidation of this derivative with atmospheric oxygen. Indole, 6-methoxyindole, and 5- and 7-azaindoles and their derivatives have been obtained in high yields from the corresponding indolines[22,113]. *N*-Acyl and *N*-benzyl substituents and halogen atoms are eliminated under the conditions of the reaction. *N*-Metallated secondary amines, for example $(C_2H_5)_2NLi$ or $C_6H_5N(CH_2C_6H_5)Li$, are known to be the most powerful donors of hydride ions and can react as reducing agents for the carbonyl group[191,192]:

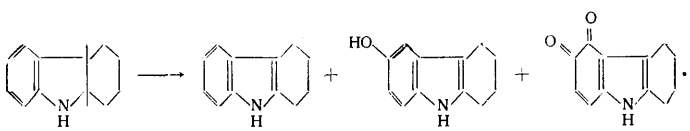
$$(C_6H_5)_2CO + C_2H_5N(Li)CH_2CH_3 \rightleftarrows (C_6H_5)_2CHOLi + C_2H_5N{=}CHCH_3$$
$$(C_6H_5)_2CO + C_6H_5N(Li)CH_2C_6H_5 \rightleftarrows (C_6H_5)_2CHOLi + C_6H_5N{=}CHC_6H_5$$

Evidently, like other *N*-metallated derivatives of secondary amines, the *N*-sodio-derivative of indoline is also a very powerful hydride ion donor, particularly since the removal of a hydride ion leads in this case to indolenine, which is converted into the more stable aromatic indole system:



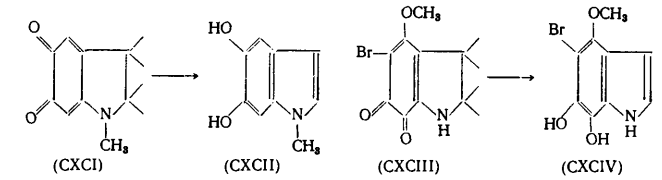
In this case atmospheric oxygen is the hydride ion acceptor[193]. 2,3-Dimethyl-7-ethylindole forms in the reaction of 2,3-dimethylindoline with aluminium anilide and ethylene in aniline at 300°C and 250 atm. It is difficult to say whether dehydrogenation or *C*-alkylation takes place first. Probably the indoline derivative is dehydrogenated as a result of the formation of an $N{-}Al_{1/3}$ derivative which tends to split off a hydride ion like N–Na derivatives[194]. The oxidation of indoline with air in the presence of heavy metal oxides yields indole[195].

When potassium nitrosodisulphonate $(NO)(SO_3K)_2$ is allowed to react with indolines, 5-hydroxyindoles and *o*-quinones of the indole series are formed together with indole derivatives; for example[196]:

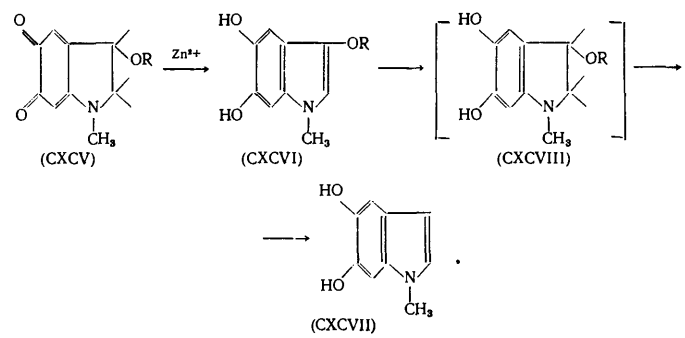


Similar reactions have been achieved with 2-phenylindoline, 2,3-dimethylindoline, and 3-methylindoline[197].

The isomerisation of aminochromes (CXCI) into 5,6-dihydroxyindole derivatives (CXCII) constitutes an unusual reaction involving intramolecular oxidation–reduction[96,198]:

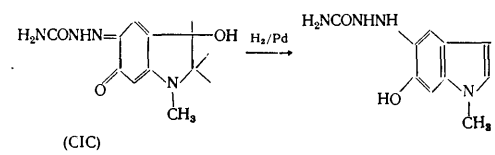


The reaction takes place under the action of Zn^{2+} and Al^{3+} ions. 6,7-Indolinequinones (CXCIII) have been isomerised to 6,7-dihydroxyindoles (CXCIV)[97]. Adrenochrome derivatives (CXCV) give rise to 3,5,6-trihydroxyindoles (CXCVI),[196,199] whose reduction with the Raney nickel alloy yields 5,6-dihydroxyindoles (CXCVII)[96]:



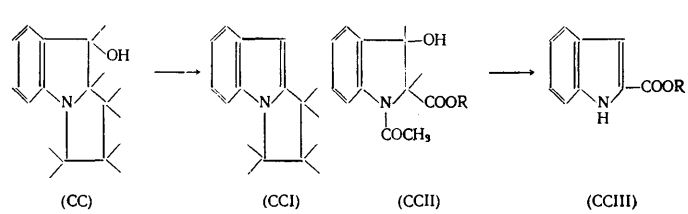
3-Hydroxyindoline derivatives (CXCVIII) probably act as intermediates. The work of Mattlock and Heacock[200] can also be quoted.

Analogous series of conversions have been described for the semicarbazone of adrenochrome (CIC)[201]:



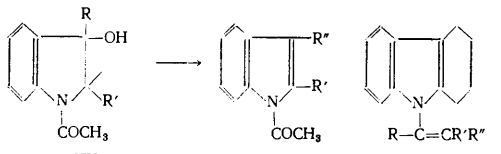
2. Dehydration of 3-Hydroxyindolines

The use of 3-hydroxyindolines for the synthesis of substituted indoles is extremely promising. Unsubstituted 3-hydroxyindoline is relatively stable in the cold to the action of acids and alkalis but on heating to 70°C it is converted into indole[71]. 3-Hydroxy-1-methylindoline is somewhat more stable to heat[71]. 3-Hydroxy-1,2-trimethylindoline (CC) has been converted into the corresponding indole (CCI) by boiling with acetic anhydride[202]:



Derivatives of 1-acetyl-3-hydroxyindoline-2-carboxylic acid (CCII) are converted into derivatives of indole-2-carboxylic acid (CCIII) under the action of mineral acids in

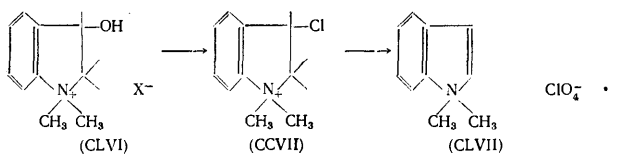
the cold[69] and on heating with alkalis[69]. Under acylation conditions compounds (CCII) give rise to *O*-acyl derivatives. A number of 2,3-disubstituted 1-acetyl-3-hydroxyindolines (CCIV) have been converted into indoles (CCV) by heating with phosphorus pentoxide in benzene[75]:



(CCIV) (CCV) (CCVI)

It has been possible to prepare indole derivatives of the type (CCVI) by heating the corresponding 3-hydroxyindolines (CLVIII) with picric acid in methanol[175].

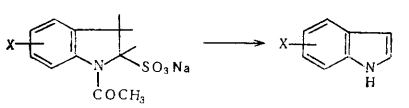
1,1-Dimethylindolium perchlorate (CLVII) has also been synthesised using the corresponding 3-hydroxyindoline derivative (CLVI)[18]:



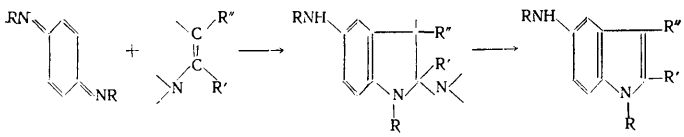
(CLVI) (CCVII) (CLVII)

However, compound (CLVI) could not be dehydrated. The 3-hydroxyindoline (CLVI) was converted into 3-chloro-1,1-dimethylindolinium chloride (CCVII), which was then further converted into the indole derivative (CLVII) by being passed through a column with Amberlite IRA-400. Evidently, the use of 3-hydroxyindolines for the synthesis of substituted indoles requires study of the method of preparation and reactivity of the *trans*- and *cis*-isomers of 2-substituted 3-hydroxyindolines.

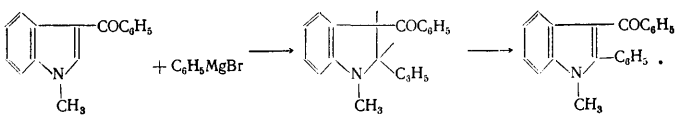
As stated above, derivatives of the sodium salts of indoline-2-sulphonic acid are converted into indoles in an alkaline medium[17]:



The range of substances which can be used for the preparation of compounds of the indole series is not restricted to derivatives of indoline, indoline-2-sulphonic acid, and 3-hydroxyindolines. There are also methods, which have been virtually not investigated, for the synthesis of 2-hydroxy- and 2-amino-indolines and for their conversion into indoles. For example, in the condensation of quinone-imines with enamines, the intermediates are 2-amino-indoline derivatives, which are converted into indoles under very mild conditions[203]:



The conversion of indoles into dihydro-derivatives with the aim of altering the reactivity of substituents in positions 2 and 3 or in order to introduce substituents in position 2 may prove very valuable. Thus 3-benzoyl-1-methyl-2-phenylindoline (CCIX) has been obtained by the reaction of 3-benzoyl-1-methylindole (CCVIII) with phenylmagnesium bromide. Its dehydrogenation over Pd/C gave 3-benzoyl-1-methyl-2-phenylindole (CCX)[204]:



(CCVIII) (CCIX) (CCX)

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THE ROLE OF THE STATIONARY PHASE IN GAS-LIQUID CHROMATOGRAPHY AND METHODS OF SORBENT SELECTION

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The possibility of controlling the selectivity of the column is one of the principal advantages of chromatography (in the first place gas-liquid chromatography) over other methods for the separation of substances, the nature of the stationary phase constituting the main factor which determines the sequence of the elution of the components from the column and the relative elution times of the peak maxima [1-3]. Furthermore, the effect of the stationary phase extends also to the mode of spreading of the zones.

1. SELECTIVITY OF THE STATIONARY PHASE AND ITS RELATION TO THE DEGREE OF SEPARATION AND THE ERROR OF THE ANALYSIS

An investigator using gas chromatography is able to solve the following groups of problems: (a) qualitative analysis of the mixture; (b) quantitative analysis of the mixture; (c) isolation of a certain amount of pure substances or fractions; (d) determination of certain physicochemical characteristics of the test system.

In qualitative analysis the degree of separation must be sufficient to obtain in the chromatogram separate peak maxima of the individual components and the displacement of these maxima under the influence of the neighbouring components should be fairly small. In quantitative analysis it is important that the analytical error associated with the quality of the separation should be within the permissible limits.

In preparative chromatography the main requirement is to ensure the necessary purity of the fraction for a sufficiently large sample volume, which is also related to the degree of separation. Finally, in the determination of physicochemical characteristics the requirements are determined by the actual problem. Regardless of the aim of the chromatographic analysis, it is desirable that the separation should be attained in a short time.

The ratio of the distance between the ordinates of the maxima to the sum of the peak widths may serve as a measure of the separation of two components. Thus the degree of separation K is defined by the formula [1]:

$$K = \frac{\Delta l}{\mu_{0.5(1)} + \mu_{0.5(2)}},$$

where Δl is the distance between the ordinates of the maxima and $\mu_{0.5(1)}$ and $\mu_{0.5(2)}$ are the peak half-widths [1,4]. K can be found from the expression

$$K = \frac{V_{R_2} - V_{R_1}}{\omega_{0.5(1)} + \omega_{0.5(2)}} = 0.212 K_c \sqrt{n}, \quad (2)$$

where V_{R_1} and V_{R_2} are the retention volumes of the components, $\omega_{0.5(1)}$ and $\omega_{0.5(2)}$ the zone widths expressed in volume units, $K_c = 2(V_{R_2} - V_{R_1})/(V_{R_2} + V_{R_1})$ is the selectivity coefficient of the column, and $n = 5.55(V_R/\omega_{0.5})^2$ the number of theoretical plates characterising the efficiency of the column. The coefficient K_c depends not only on the nature of the stationary phase but also on the fraction of the column volume occupied by this phase. This follows from the equation

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{V_0}{V_{R_2} - V_{R_1}},$$

where $k_c = 2(V'_{R_2} - V'_{R_1})/(V'_{R_2} + V'_{R_1})$ is the selectivity coefficient of the stationary phase, V'_{R_1} and V'_{R_2} are the reduced retention volumes of the components, and V_0 is the gas volume (the retention volume of the non-sorbed substance).

Thus in order to achieve a satisfactory degree of separation of a two-component mixture, it is necessary that the zone spreading should be small and that the difference between the retention volumes, which is determined by the selectivity, should be large. By selectivity one should understand the property of the sorbent which gives rise to the relative displacement of the chromatographic peaks of the components.

The relation between the selectivity of the stationary phase and the degree of separation follows from Eqns. (2) and (3). However, K cannot be a complete characteristic of the conditions of analysis (determining whether or not they are satisfactory), since it does not determine unambiguously the magnitude of the analytical error (in quantitative analysis), the purity of the fraction (in the isolation of the components for preparative purposes), etc. Yet another important factor is the composition of the binary mixture to be separated. Furthermore, when the peaks are not separated completely, significant differences arise also in the calculation of K. Indeed, as a result of the mutual overlapping of the zones of neighbouring components, the peak width and sometimes also the value of Δl change (this has a particularly pronounced effect on the results of qualitative analysis) and therefore K determined from the general elution curve will differ from the value calculated from the individual curves for the components (the latter value will be called the effective separation factor K_{eff})[5]. It is frequently impossible to determine the peak width at the height necessary for the calculation of K.

Therefore, in order to estimate this degree of separation of overlapping peaks, it is desirable to employ the degree of separation defined by[5,6]

$$\psi = \frac{h_2 - h_{\min}}{h_2},$$

where h_2 is the height of the smaller peak and $h_{\min}$ the ordinate of the minimum between the peaks (Fig. 1). It has been shown[5-7] that the factor ψ, which varies steadily from 0 to 1 with K_{eff} and the ratio m of the heights of the neighbouring peaks, has important advantages over the previously employed factor $\theta = f/g$ (Fig. 1)[4,8,9], where f is the distance along the normal to the base line from the minimum to the point of intersection with the straight line joining the maxima and $g = f + h_{\min}$.

The relation between the degree of separation and the error of quantitative analysis (or the purity of the fraction in preparative chromatography) has been examined[5,10,11,12].

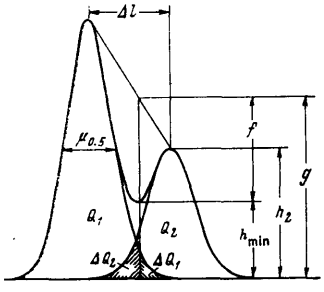


Fig. 1. Partial separation of peaks.

The column selectivity necessary to attain the required accuracy of the analysis (for specified column efficiency and peak ratio m) can be found from a nomogram[7].

Thus the selectivity of the stationary phase, which is the principal chromatographic characteristic of the latter, determines directly (other conditions being equal) the degree of separation and the error of the analysis of a two-component mixture.

2. INTERMOLECULAR INTERACTIONS IN THE COLUMN AND RETENTION CHARACTERISTICS

Raoult's law holds for an ideal dilute solution of a volatile substance:

$$p = xp^0, \tag{5}$$

where p^0 is the vapour pressure of the pure solute, p the vapour pressure of the solute over the solution, and x its mole fraction in the solution. In order to take into account positive and negative deviations from Raoult's law, the activity coefficient γ is introduced into the right-hand side of Eqn. (5). Then the combined Dalton–Raoult law can be represented by the formula

$$yP = \gamma xp^0, \tag{6}$$

where P is the total pressure in the system and y the mole fraction of the given substance in the gas phase.

According to Henry's law,

$$a = \Gamma c, \tag{7}$$

where a is the concentration of the solute in the liquid phase, c the concentration in the gas phase, and Γ Henry's constant; one can write

$$\Gamma = \frac{a}{c} = \frac{N_L + a}{N_G + c} \cdot \frac{x}{y} \simeq \frac{N_L}{N_G} \cdot \frac{x}{y}, \tag{8}$$

where N_L is the number of moles of the stationary liquid per unit volume of the liquid phase and N_G the number of moles of the carrier gas per unit volume of the gas phase. Since

$$P = N_G RT,$$

where R is the gas constant and T the absolute temperature, it follows from Eqns. (6)–(9) that

$$\Gamma = \frac{N_L RT}{\gamma p^0} = \frac{\rho RT}{\gamma p^0 M}, \tag{10}$$

where ρ and M are the density and molecular weight of the stationary liquid.

Thus the following expression can be obtained from Eqn. (10) for the specific retention volume V_g^T at a temperature T:

$$V_g^T = \frac{\Gamma}{\rho} = \frac{RT}{\gamma p^0 M}. \tag{11}$$

The specific (absolute) retention volume V_g is

$$V_g = \frac{273\,R}{\gamma p^0 M}. \tag{11a}$$

Next we establish the relation between Henry's constant and the principal thermodynamic characteristics of the system. The equilibrium between the gas and the liquid presupposes the equality of the corresponding free energies, $F_G = F_L$, where

$$F_G = F_G^0 + RT \ln c \quad \text{and} \quad F_L = F_L^0 + RT \ln a \tag{12}$$

(F_G^0 and F_L^0 are the standard free energies in the gas and liquid phases corresponding to a concentration of one mole per unit volume)†. Hence we have [14] the following equation:

$$\Delta F^0 = RT \ln \Gamma \tag{13}$$

or

$$\Gamma = e^{\Delta F^0/RT} = e^{-\Delta S^0/R}\, e^{\Delta H^0/RT} = \Gamma_S\, \Gamma_H, \tag{14}$$

where ΔS^0 is the entropy change per mole of substance on transition from the gas to the liquid phase and ΔH^0 the corresponding enthalpy change.

It follows from Eqn. (14) that the heat of solution Q, numerically equal to ΔH^0, can be determined from the following equation:

$$\frac{d \ln \Gamma}{d(1/T)} = \frac{\Delta H^0}{R}, \tag{15}$$

using a $\lg \Gamma$ (or $\lg V_R'$, $\lg V_N$, or $\lg V_g$)[4] plot. Evidently the following equation holds for the relative retention volume V^{rel}:

$$\frac{d \ln V^{rel.}}{d(1/T)} = \frac{\Delta Q}{R}, \tag{16}$$

where ΔQ is the difference between the heats of sorption of the component being analysed and a standard. If the enthalpy change is determined on the basis of the relation between the logarithm of the specific retention volume and the reciprocal of the absolute temperature [$d \ln V_g/d(1/T) = \Delta H'/R$], the following equation can be obtained [15,16]:

$$\Delta H' = \Delta H^0 + RT - \frac{RT^2}{\rho}\frac{d\rho}{dT} = 2{,}303R\, b \left(\frac{T}{T+C}\right)^2 + R\, T \left(1 - \frac{\beta T}{\rho}\right), \tag{17}$$

where b is the slope of the plot of $\lg \Gamma$ against $1/(T + C)$, C a constant, ρ the density of the stationary phase (g ml^{-1}), and β the constant in the relation $\rho = \alpha - \beta T$.

The contribution which the activity coefficient makes to the thermodynamic characteristics can be estimated for Eqns. (10) and (13). It has been shown [16-18] that

$$\frac{d \ln V_g}{dT} = -\frac{d \ln \gamma}{dT} - \frac{d \ln p^0}{dT} = -\frac{\lambda - \Delta h}{RT^2}$$

and

$$\frac{d \ln V_g}{d(1/T)} = \frac{\lambda - \Delta h}{R} = \frac{\Delta H'}{R}, \tag{18}$$

where λ is the latent heat of evaporation and Δh the excess enthalpy of solution (numerically equal to the heat of mixing) due to the deviation of γ from unity.

Adlard [19] showed that in the determination of the activity coefficient at infinite dilution γ^∞ from chromatographic data account must be taken of the non-ideality of the gas phase (by the method of Ashworth and Everett):

$$\lg \gamma^\infty = \lg \gamma + \frac{(B - v)(P - p^0)}{2.303\, RT}, \tag{19}$$

where B is the second virial coefficient in the equation of state of the gas and v the molar volume of the liquid solute.

By analogy with the derivation of Eqns. (13) and (14), one can write:

$$\lg \gamma^\infty = \frac{\Delta h}{RT} - \frac{\Delta s}{R}, \tag{20}$$

where Δs is the excess entropy of solution [17] and

$$\Delta h = R \frac{d \ln \gamma^\infty}{d(1/T)}. \tag{21}$$

The activity coefficient and hence the thermodynamic potentials are determined by the sum of the attraction and repulsion forces acting between the molecules in the chromatographic column. The total energy of the interaction of molecules in the liquid phase [1,14,20-23] consists of the energy of dispersion, induction, and orientation forces, the energy of specific interaction, and also the work expended to pull apart the solvent molecules‡.

As a result of the low concentration of the solute, the interaction between its molecules is usually disregarded although it has been shown in some studies [25] that in a number of cases the concentration effect does influence the results of the chromatographic process. Dispersion forces are of decisive importance in the interaction between the molecules of a non-polar solvent and a non-polar solute. They are due to the presence of virtual dipoles which give rise to an electric field inducing dipole moments in other molecules. Orientation forces arise between molecules with permanent dipoles due to their tendency to attain the orientation with the lowest energy. For example, orientation interaction occurs between sulphides and tricresyl phosphate molecules.

Induction forces act between the permanent dipole of one substance and the induced dipole of another. In particular, dipoles are induced in unsaturated and aromatic hydrocarbons. Although the energy of induction interaction is low, amounting to only 5–10% of the energy of dispersion interaction, it can nevertheless be sufficient to ensure the required chromatographic separation.

Specific forces include the hydrogen bond formed between a hydrogen atom and fluorine, oxygen, nitrogen, or chlorine atoms, donor–acceptor interaction, and complex formation.

The overall energy of interaction E between solvent and solute molecules can be represented by the following relation [22] when account is taken of dispersion, orientation, and induction forces:

$$E = -\frac{1}{r^6}\left(\frac{2}{3}\frac{\mu_1^2\mu_2^2}{kT} + \mu_1^2\alpha_2 + \mu_2^2\alpha_1 + 3\pi h \alpha_1\alpha_2 \frac{\nu_1\nu_2}{\nu_1 + \nu_2}\right), \tag{22}$$

where r is the distance between the molecules, μ_1 and μ_2 are the dipole moments, k is the Boltzmann constant, α_1 and α_2 are the polarisabilities of the solvent and solute molecules, h is the Planck constant, and ν_1 and ν_2 are the frequencies. The first term on the right-hand side of the equation characterises the orientation forces, the second and third terms the induction forces, and the fourth term the dispersion forces.

In his analysis of aliphatic acid esters on a column with an Apiezon grease, James [26] found that the dispersion forces decrease with increase in the branching and decrease of the molecular weight of the substances to be separated, because the esters of branched and unsaturated acids move in the column at a higher rate than those of saturated acids. It was shown that the dispersion forces are also influenced by the position of the double bond and the configuration of the molecule, in particular *trans*-isomers have somewhat higher retention volumes than *cis*-isomers

† The questions involved in the selection of the standard state have been examined in detail by James et al. [13]

‡ Kovats and Weiss [24] determined the contribution of these terms on the basis of retention indices [see Eqn. (46)].

and can be separated from the former when the efficiency of the column is equivalent to 4000 theoretical plates.

An example of the effect of induction forces is provided by separation using poly(ethylene glycol) and poly(propylene glycol) adipates as the stationary phases, described in James's paper quoted above. These liquids polarise the double bonds of unsaturated acid esters and increase the retention volumes of the latter, the positions of the double bonds and stereoisomerism being unimportant.

A very interesting example of the separation of components under the influence of induction forces is the chromatographic analysis of a mixture of thiophen and diethyl sulphide, using tricresyl phosphate as the stationary phase[27]. The boiling point and the dipole moment of diethyl sulphide are larger than those of thiophen, but, as a result of the high polarisation of thiophen which has aromatic properties, the latter is eluted after diethyl sulphide (here, as in the preceding example, donor–acceptor interaction evidently also takes place). On a column with a non-polar phase the components are of course eluted in the reverse order.

Hydrogen bonds are formed, in particular, between water and glycerol molecules, which permits the use of glycerol for the analysis of mixtures containing water[28]. When polyethylene oxide is used in the presence of amines, primary amines are strongly retarded and secondary amines less so. Tertiary amines have the smallest retention volumes due to the absence of the hydrogen bond with the stationary phase[29]. Evidently the role of the hydrogen bond in the overall energy of interaction between substances decreases with their molecular weight. Therefore the use of diglycerol or a polyester resin[21,30] as the stationary liquid in the analysis of alcohols makes it possible to elute ethanol first and methanol second.

Chromatographic separation can be achieved also with the aid of stationary phases which form complexes of varying stabilities with the components to be separated. Thus solutions of silver nitrate are widely used in the analysis of unsaturated hydrocarbons[31–35] and salts of aliphatic acids in the separation of amines[29]. The chromatogram obtained in the separation of gases on a column with a solution of silver nitrate in glycol shows that saturated hydrocarbons are eluted as a single peak, which is followed by the elution of the unsaturated compounds.

A novel method for the analysis of light gases has been described by Zhukhovitskii et al.,[36] who used blood as the stationary liquid for the selective retention of oxygen.

The theory of gas chromatography on columns with complex-forming phases (using silver nitrate solutions as an example) has been examined by a number of investigators[33,34]. In particular, Genkin showed[33] that Henry's constant can be determined from the equation

$$\Gamma = \Gamma^0 + \varkappa\Gamma^0 \; c_b \; , \qquad (23)$$

where $\varkappa = c_{ab}/c_a c_b$ is the stability constant of the complex, Γ^0 Henry's constant for the solvent containing the complex-forming agent, c_b the concentration of the complex-forming agent, and c_{ab} the concentration of the complex.

The work expended to pull apart the solvent molecules merits special examination. It has been shown[14] that, when a number of simplifying assumptions are made, this work A can be defined thus:

$$A = 4\pi r^2 \qquad (24)$$

where r is the radius of the solute molecule and σ the surface tension of the solvent. A increases with the size of the molecule in experiments with polar stationary phases and also with the polarity of the phases. Since A and E vary in the opposite sense, it has been concluded[37] that in the dissolution of non-polar substances the total interaction energy E decreases with increasing polarity of the solvent due to an increase of the work A; on the other hand, when polar substances are dissolved, the total energy increases with the polarity of the solvent. In this connection it is evident that for certain weakly polar substances the above effects can cancel out, resulting in an invariant Henry's constant (in the work quoted ethyl ether served as an example of such a weakly polar substance).

The role of the work A has been investigated in detail by Burrows and Preece[15]. If ΔE_A is the energy required to remove (at a constant temperature) the solute molecules from "holes" in the solvent and ΔE_C the energy liberated when the "holes" are filled up by solvent molecules (consequently ΔE_C is the energy of formation of the "holes"), the heat of sorption can be determined from the relation

$$\Delta H' = \Delta E_A - \Delta E_C + RT \; , \qquad (25)$$

where the last term characterises the excess work which must be performed.

The following expression holds for ΔE_A:

$$\Delta E_A = \frac{N(\epsilon_b - \epsilon_i)}{J} \; , \qquad (26)$$

where N is the Avogadro number, $\epsilon_b = \frac{1}{2}mv^2 \simeq \frac{1}{2}m(2\pi\nu r)^2$ the vibration energy of the solute molecule (when its mass is m and velocity v), r the radius of the "hole", ϵ_i the internal potential energy of the solvent molecule, and J the mechanical equivalent of heat (erg cal^{-1}). The radius of the "hole" can be determined as a function of Henry's constant in the following form:

$$r = 5.66 \times 10^7 \Gamma \, (\Delta E_A/2T)^{1/2} \cdot \exp(-\Delta E_A/RT) \qquad (27)$$

and

$$\Delta E_C = \Delta E_A - (\Delta H' - RT) = 18.1 r^2 (n+1)\sigma \; , \qquad (28)$$

where σ is the surface tension and n the constant in the relation between σ and temperature T; $18.1 = \pi N/J$.

An empirical relation derived by Burrows and Preece[15] for dinonyl phthalate (at 80°C) is of the form

$$\lg \Gamma = 0.62\,\Delta E_A - 7.93 \; ,$$

where ΔE_A is expressed in kcal mole^{-1}. The radius of the "hole" was found to be about 3.4 Å.

The effect of the entropy factor on the chromatographic process has been investigated in a number of studies[15,17,37,38]. It has been shown that very often the separation of the sample components is in fact due to the differences in their entropies of solution. Korol'[38] obtained the following formula for the determination of the excess entropy of solution Δs:

$$\Delta s = \beta C_1 \ln\frac{1}{M} + C_2 \; , \qquad (30)$$

where β is a function of the heat of solution and the rigidity of the solvent and solute molecules ($\beta = 0$ corresponds to complete filling of the "holes" while maintaining the structure of the stationary phase), M the number of "holes" per mole of substance, and C_1 and C_2 are constants. Zhukhovitskii et al.[36] also examined the components of the excess entropies: the entropy of migration of the centre of mass

of the molecule and the entropy of rotation of the molecule and its individual parts, the first term being calculated from the excess entropy of a non-polar spherical molecule (carbon tetrachloride) in solution in a saturated hydrocarbon.

In concluding this section, the possibility of rapid chromatographic separation of high-boiling polar compounds may be pointed out. Since the low vapour pressure of such substances in the pure state is due to molecular association, the retention time is sharply reduced in chromatographic analysis on a column with a non-polar phase, where the interactions between solute molecules may be neglected and only dispersion forces act between solvent and solute molecules[5,38]. For example, in experiments on a column with n-heptadecane (at 22°C) the peak of ethylene glycol, which has a boiling point of 197.2°C, is recorded between the peaks due to hexane and heptane, which boil at 68.7° and 98.4°C respectively. Here of course particular attention must be paid to the selection of a carrier with low adsorption activity§. This procedure is also used in the analysis of polar substances by gas-adsorption chromatography[39].

Finally yet another peculiarity, which occurs in the analysis of polar substances on columns with polar stationary phases, may be noted. It has been shown[40-42] that here the absorption of the components being separated is accompanied by their adsorption on the surface of the liquid. Here the retention volume should be defined as the sum of two terms, one of which is the function of Henry's absorption constant and depends on the amount of the liquid phase and the other is a function of the surface excess Γ and depends on the area.

3. RELATION BETWEEN MOLECULAR STRUCTURE AND SORPTION PROPERTIES

One of the first attempts to establish the relation between the activity coefficient and the structure of solvent and solute molecules was made by Pierotti et al.,[43] who proposed the so-called "structural block" method. According to their concept, in which the interactions between the functional groups and alkyl radicals of both molecules are considered, the following relation should hold:

$$\lg \gamma = A + \frac{B - n_C}{n'_C} + \frac{C}{n_C + C'} + D\,(n_C - n'_C)^2 + \frac{F}{n'_C + F'} \quad , \qquad (31)$$

where n_C is the number of methyl and methylene groups in the solute molecule, n'_C the number of the corresponding groups in the solvent molecule, and A, B, C, D, F, C', and F' are constants[20]. A linear relation between $\lg \gamma$ and the number of carbon atoms in the solute molecule follows from Eqn. (31) for the analysis of homologues on a column with a definite phase. In the choice of stationary phases and also in the identification of the components of the mixtures being analysed, relations between retention volumes and the number of carbon atoms in the molecule, the boiling point T_b, or the vapour pressure p^0, which are valid within the limits of a single homologous series of solutes, are widely used. Herington[44] showed that, for the logarithm of the retention volume defined by

$$\lg V^{rel} = \lg \frac{p_1^0}{p_2^0} + \lg \frac{\gamma_1}{\gamma_2} \quad , \qquad (32)$$

where subscript 1 refers to the component being analysed and subscript 2 to a standard, the following relations hold,

$$\begin{aligned} \lg V^{rel} &= a + b\ n_C, \\ \lg V^{rel} &= a_T + b_T\ T_b \quad , \\ \lg V^{rel} &= a_s - b_s \lg p^0 \quad , \end{aligned} \qquad (33)$$

where a, b, a_T, a_s, and b_s are constants whose values depend on the nature of the stationary phase, the working temperature, and the homologous series of the substances being separated.

There is a linear relation also between the retention volumes of the components of a given homologous series on two columns with different stationary phases[45]. Fig. 2 shows that in separation on a column with a non-polar phase the straight lines corresponding to different homologous series are significantly closer to one another than in separation on a polar phase[46].

The selectivity coefficient k'_s for adjacent components of the same homologous series is of course constant, since the heat of solution Q is an additive quantity:

$$Q = Q_0 + Q_{CH_2}\ n_C \quad , \qquad (34)$$

where Q_0 and Q_{CH_2} are constants.

Zhukhovitskii and coworkers[1,47] proposed a more general relation than Eqn. (33):

$$\lg V^{rel} = a' + b' \frac{T_b}{T} \quad , \qquad (35)$$

which holds over a definite range of working temperatures T. Relations between the retention volumes and other physicochemical characteristics of the substances to be separated,

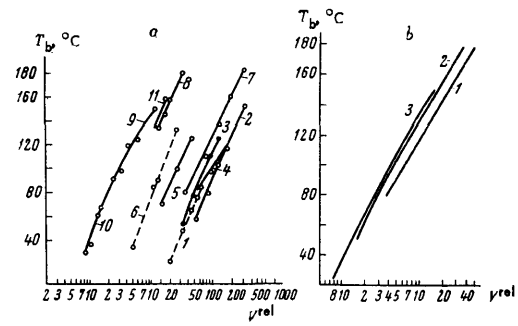


Fig. 2. Variation of the relative retention volumes with the boiling points[44]:
a) column with di(β-cyanoethyl) ether; temperature 67°C: 1) aldehydes; 2) ketones; 3) acetates and formates; 4) alcohols; 5) acetylenes; 6) ethers; 7) alkylbenzenes; 8) alkylcyclohexanes; 9) straight-chain saturated hydrocarbons; 10) olefine; 11) alkylcyclopentanes;
b) column with Fluorolube; temperature 100°C: 1) alkylbenzenes; 2) cycloalkanes; 3) straight-chain saturated hydrocarbons, methylparaffins, and olefins.

§ Without considering in detail the questions associated with the choice of the solid carrier, it may be noted that the interfering effect of the latter on the retention characteristic is often very considerable.

for example refraction[48], the parachor[49], dipole moment[50], etc., are also used in practice. Anvaer et al.[14] showed that, when the work expended to remove equal volumes of the solvent and solute (saturated hydrocarbons) is the same the heat of solution Q should be related to the heat of evaporation λ_v as follows:

$$Q = \frac{\lambda_v}{V_1} V_2 \ , \qquad (36)$$

where V_1 and V_2 are the molar volumes of the solvent and solute. Consequently a linear relation between the logarithm of the reduced retention characteristic and V_2 should hold within the limits of each homologous series.

A method for the calculation of retention parameters, based on the physicochemical characteristics of the solvent and solute, has been proposed by Martire[51], who started with Hildebrand's equation:

$$\ln \gamma = \frac{V_2}{R \cdot T} \Phi_1^2 (\delta_1 - \delta_2)^2 \ , \qquad (37)$$

where V is the molar volume, Φ_1 the volume fraction of the solvent in the solution, $\delta = \sqrt{\lambda_v / V}$ is a solubility parameter, subscript 1 refers to the solvent and subscript 2 to the solute. Since Eqn. (37) holds only for non-polar molecules and for positive deviations from Raoult's law, Martire added appropriate terms and obtained the relation

$$\ln \gamma = \frac{V_2}{R \cdot T} \Phi_1^2 [(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 - C] \ , \qquad (38)$$

where $\omega \simeq \mu^2/V$, μ is the dipole moment, and C characterises the negative deviation from Raoult's law, $C = k(V_2/\delta_2)$ and k depending only on the nature of the solvent.

Anvaer[52] based his treatment on a familiar model, according to which the transfer of a molecule with radius r and dipole moment μ from the vacuum into a dielectric with dielectric constant ϵ involves an energy gain:

$$\Delta E = \frac{2}{9} \frac{\mu^2}{r^3} \left(1 - \frac{1}{\varepsilon}\right) \ . \qquad (39)$$

If it is assumed that the work ΔE corresponds to the free energy change, there is a linear relation between the logarithm of Henry's constant (or the logarithm of the relative retention volume) of any component and $1/\epsilon$. This hypothesis has been used[52] to classify stationary phases.

It is interesting to examine the variation of sorption characteristics within a homologous series of stationary liquids. According to the Clausius–Mosotti equation, the molecular polarisation P_{mol} is

$$P_{mol} = \frac{\varepsilon - 1}{\varepsilon + 2} V_1 = \frac{4}{3} \pi N \left(\alpha + \frac{\mu^2}{3kT}\right) \ , \qquad (40)$$

where $\alpha = \alpha_{at} + \alpha_{el}$, α_{at} is the atomic polarisability, α_{el} the electronic polarisability, $\alpha_{or} = \mu^2/3kT$ the orientation polarisability, and k is the Boltzmann constant. Using the equation $\frac{4}{3}\pi N \alpha_{el} = M_R$, where M_R is the molecular refraction, Sakharov[53] obtained the relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{M_R}{V_1} + \frac{4}{9} \frac{\pi N}{kT} \frac{\mu^2}{V_1} \ . \qquad (41)$$

The ratio M_R/V_1 and the dipole moment are almost constant within a homologous series and therefore, in accordance with Onsager's equation, we have

$$\Delta E = \frac{\mu^2}{r^3} \frac{\varepsilon - 1}{2\varepsilon + 1} \ , \qquad (42)$$

which is more accurate than Eqn. (39), since the mutual polarisation of molecules is taken into account. Sakharov showed that the following equation holds for a particular component:

$$\lg \Gamma \simeq A \frac{1}{V_1} + B \ . \qquad (43)$$

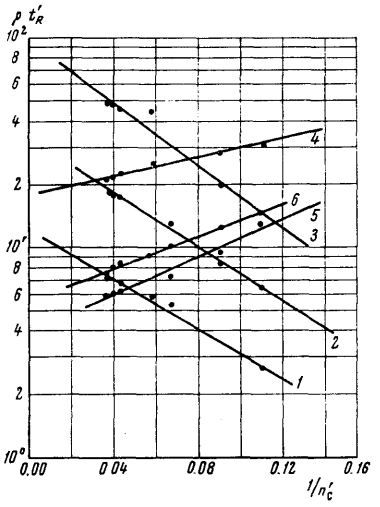


Fig. 3. Variation of the product of the reduced retention time t'_R and the density of the stationary phase ρ with the reciprocal of the number of carbon atoms in the molecule of the stationary phase (dialkyl phthalates); temperature 50°C:
1) n-hexane; 2) n-heptane; 3) n-octane; 4) benzene; 5) methanol; 6) ethanol.

Indeed it has been shown in the work of Chovin and Ducros[54], Petsev and Dimitrov[55], and the author of the present review[56,57] that the relation between $\lg\Gamma$ and the number of carbon atoms n'_C in the stationary phase molecule is non-linear, although it does approach linearity for fairly high values of n'_C. However, the plot in Fig. 3 shows that the relation between $\lg\Gamma$ and $1/n'_C$ is in fact linear.

4. CLASSIFICATION OF STATIONARY PHASES

A number of investigators have based the classification of stationary phases on the relation between the polarity and the retention characteristics of specified substances. Rohrschneider[58] placed the stationary phases along the abscissa axis (Fig. 4) so as to obtain a linear variation of the logarithm of the retention volume of divinyl relative to butane on transition from one phase to another. A polarity of zero was attributed to squalane and a polarity of 100 to di(β-cyanoethyl) ether. This made it possible to characterise stationary phases by the corresponding polarity indices.

In other investigations[59–62] almost the same method of classification was used but with the difference that acetylene and ethane, methanol and butane, two straight-chain saturated hydrocarbons, etc. were used as standards. Sakharov[53,63] showed that all these methods follow from the general relation

$$\lg V^{rel} = B_1 \lg V_{st}^{rel} + B_2 \ , \qquad (44)$$

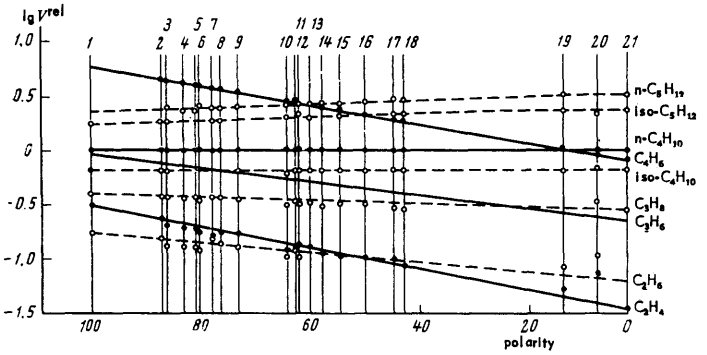


Fig. 4. Relation between the retention volume of a substance (relative to n-butane) and the polarity of the stationary phase[53]:
1) di(β-cyanoethyl) ether; 2) *N*-methylacetyl-β-aminopropionitrile; 3) *N*-formylmorpholine; 4) propylene glycol carbonate; 5) ethyl cyanoacetate; 6) dimethylformamide; 7) poly(ethylene glycol) 600; 8) glycol sulphite; 9) acetonylacetone; 10) benzyl cyanide; 11) diethylformamide; 12) diethylcyanamide; 13) propylene glycol sulphite; 14) epoxypropylmorpholine; 15) 1,3-butylene glycol sulphite; 16) *N*-β-hydroxypropylmorpholine; 17) dibenzyl ether; 18) dibutylformamide; 19) 1-chlorooctadecane; 20) silicone oil; 21) squalane.

where V^{rel} is the relative retention volume of a particular component, V_{st}^{rel} the relative retention volume of the standard, and B_1 and B_2 are constants; B_1 characterises the polarity of the substance being analysed and lg V_{st}^{rel} serves as the characteristic of the polarity of the solvent (for the latter one can use not only the logarithm of the retention volume of the standard but also some other suitable quantity in particular $1/\epsilon$). Sakharov pointed out that the correct choice of the standard can significantly reduce the error in the determination of retention characteristics; it is recommended that a substance belonging to the same class of compounds as the component being analysed should be selected as the standard.

The above method of classification has important advantages because it greatly simplifies the choice of stationary liquids for the separation of particular mixtures and also for the identification of unknown components. However, it also has a number of disadvantages, associated with failure to take into account the entire wide variety of intermolecular interactions between stationary phases and the substances being separated.

Plots of the retention index [see Eqn. (46)] against the polarity of the stationary phase have been quoted by Chovin[54]. Lazarse and Roumazielles[65] showed that the relation between the polarity and the ratio of the reduced retention volumes of straight-chain saturated hydrocarbons (with $z + 1$ and z carbon atoms in the molecules) multiplied by the absolute temperature of the column is of the same type.

The method proposed by Brown[66] is based on a characteristic of only the donor–acceptor properties of stationary phases. On a triangular graph, each phase has a point with the coordinates

$$\frac{V_n}{V_n+V_a+V_d}, \frac{V_a}{V_n+V_a+V_d}, \text{and} \frac{V_d}{V_n+V_a+V_d},$$

where V_n, V_a, and V_d are respectively the retention volumes of a non-polar substance and an electron acceptor and donor on a column with the given phase. n-Hexane, ethanol, and 2-butanone and also n-decane, 1,1,2-trichloroethylene, and dioxan have been used as the standard substances for the determination of the properties of the phases. The position of the point relative to the vertices of the triangle can serve as a characteristic of the phase.

5. METHODS OF SELECTION OF STATIONARY PHASES

In selecting the stationary phase to solve a particular analytical problem the greatest attention is of course given to the selectivity of the phase. Furthermore, there are additional requirements, which include: (1) the absence of chemical interaction with the substance to be separated, the solid carrier, the column wall, and the carrier gas; (2) chemical stability under operating conditions; (3) low vapour pressure under operating conditions; (4) low viscosity. It is desirable that the phase should be readily available and that it should contain the minimum amount of impurities.

Depending on the composition of the mixture to be analysed, the following aspects of selectivity should be considered; (1) selectivity as the capacity to separate any two components; (2) selectivity as the capacity to separate the components of a single homologous series; (3) selectivity as the capacity to separate the components of two (or several) homologous series[67].

The selection of the stationary phase for the separation of two components must be based in the general case on the retention characteristics of the substances taken from the literature[1,9,68–74] or determined experimentally. In the analysis of homologues the principal criterion in the selection of the stationary phase is the coefficient b in the equa-

tion relating the logarithm of the reduced retention characteristic and the number of carbon atoms in the molecule [see Eqn. (33)]. For adjacent homologues, the selectivity coefficient k_s of the stationary phase is

$$k_s = 2\frac{10^b - 1}{10^b + 1} \quad (45)$$

i.e. the selectivity is greater the larger is b.

If instead of the retention volume one uses[75-78] as the retention characteristic the retention index I, defined by

$$I = r\frac{\lg V'_{R_x} - \lg V'_{R_z}}{\lg V'_{R_{(z+r)}} - \lg V'_{R_z}} + z \quad (46)$$

(a quantity larger by a factor of 100 was used by Kovats and coworkers[75-78]), where V'_{R_x}, V'_{R_z}, and $V'_{R_{z+r}}$ are the reduced retention volumes of the substance analysed and straight-chain saturated hydrocarbons with z and $z + r$ carbon atoms in the molecules, then the selectivity, considered as the capacity to separate homologues, can be estimated as the difference between the retention indices of adjacent homologues:

$$\Delta I = b/b_p \ , \quad (47)$$

where the coefficient b_p refers to the homologous series of straight-chain saturated hydrocarbons (paraffins).

If the problem is to separate the components of two homologous series, it is necessary to use a stationary phase which causes a shift of the $\lg V^{rel} - n_C$ linear plot for one series relative to that for another, and the shift can serve as a measure of the selectivity of the phase.

Bayer and Rock[79] introduced a selectivity factor δ, which is equal to the ratio of the reduced retention characteristics of two substances belonging to different homologous series and having different boiling points (or more precisely substances which have the same vapour pressures at the working temperature):

$$\delta = \frac{V'_{R_2}}{V'_{R_1}} = \frac{p_1^0\gamma_1}{p_2^0\gamma_2} = \frac{\gamma_1}{\gamma_2} \ . \quad (48)$$

The values of δ for various sorbents and classes of substances to be separated, determined by graphical interpolation, have been widely used[68,80].

It can be shown that the relation between the factor δ and the selectivity coefficient k_s is

$$k_s = 2\frac{10^b - 1}{10^b + 1} = 2\frac{\delta\left(\frac{p_1^0}{p_2^0}\right)^{b_s} - 1}{\delta\left(\frac{p_1^0}{p_2^0}\right)^{b_s} + 1} \quad (49)$$

when $\delta(p_1^0/p_2^0)^{b_s} > 1$, which corresponds to the elution of the components in the sequence 1–2, and

$$k_s = 2\frac{\frac{1}{\delta}\left(\frac{p_2^0}{p_1^0}\right)^{b_s} - 1}{\frac{1}{\delta}\left(\frac{p_2^0}{p_1^0}\right)^{b_s} + 1} \quad (50)$$

when $\delta(p_1^0/p_2^0)^{b_s} < 1$, which corresponds to the reverse sequence. Instead of $(p_2^0/p_1^0)^{b_s}$, one can use the expression $10^{b\Delta T_b}$, where ΔT_b is the difference between the boiling points of the components to be separated.

Thus the phase with the greatest or smallest factor δ (i.e. the phase which ensures the highest value of the coefficient k_s) is the most effective for the separation of a pair of substances belonging to different homologous series.

Suppose, for example that such pairs are heptane–hept-1-ene and decane–benzene. Fig. 5 shows the relation between the logarithms of the reduced retention volumes and the boiling points of straight-chain saturated hydrocarbons, straight-chain olefins, and alkylbenzenes in analysis on columns with squalane and adiponitrile[67]. It is evident from the graph that δ for olefins and saturated hydrocarbons is 1.90–1.95 on adiponitrile and 1.0 on squalane.

Adiponitrile is one of the most selective phases for the separation of the above classes of compounds. Calculation of the coefficient k_s shows that it is 0.15 for the non-polar phase and 0.53 for the polar phase and thus the latter is preferable. On the other hand, because of the considerable difference between the boiling points of benzene and decane, in their separation the non-polar phase with δ = 1.2 is preferable to the polar phase with δ = 16.0, since in the first case we have k_s = 1.8 and in the second 0.3.

It follows from the above example that the choice of the best phase for the separation of any pair of substances can be based on the tabulated values of δ.

Similarly it is possible to select optimum phases for the analysis of 3- and 4-component mixtures of substances belonging to two homologous series[67]. Thus if substances 1 and 2 belong to one series and substance 3 to another,

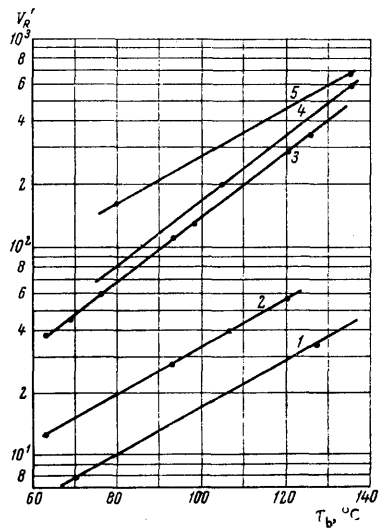


Fig. 5. Relation between the reduced retention volumes and the boiling points of hydrocarbons on columns with squalane and adiponitrile at 40°C:
1) straight-chain saturated hydrocarbons, adiponitrile; 2) straight-chain olefins, adiponitrile; 3) straight-chain saturated hydrocarbons and straight-chain olefins, squalane; 4) aromatic compounds, squalane; 5) aromatic compounds, adiponitrile.

the optimum value of δ for a phase which would ensure elution in the sequence 1–3–2 is

$$\delta = \frac{(p_3^0)^{b_s}}{(p_1^0\ p_2^0)^{0.5 b_s}} \quad \text{or}$$

$$\lg \delta = 0.5\, b_\tau (T_{b_1} + T_{b_2} - 2T_{b_3}) \qquad (51)$$

it being assumed that the values of b_s are similar for both series.

Since the order of elution is influenced both by the selectivity of the phase and the vapour pressures of the components, evidently by itself a certain degree of selectivity of the phase in relation to one of two homologous series does not ensure the separation of these components. Thus mixtures of straight-chain saturated hydrocarbons and alkylbenzenes have been separated on columns with technical fractions of aliphatic acids as the stationary phases[81]. The corresponding chromatograms are shown in Fig. 6. Whereas on the column with the light acid fraction the benzene peak is superimposed on the heptane peak, when the vat residue is used the retention volume of benzene increases and the latter is eluted after heptane. Even greater selectivity in relation to aromatic hydrocarbons is shown by the middle acid fraction on a column in which benzene is eluted together with octane.

Thus it is evident from the chromatograms that, although the middle acid fraction is in fact more selective, the vat residue or even the non-polar liquid paraffin are more suitable for a clear separation of saturated hydrocarbons and alkylbenzenes (Fig. 7).

In the separation of components belonging to two homologous series approximately equal separation factors for all pairs of peaks can be achieved in two ways[82]:

a. By using a selective sorbent characterised by

$$k_{s1,2} = \frac{10^{b_s(m+1)} - 1}{10^{b_s} - 1} k_{s1} \text{ and } k_{s1} \simeq k_{s2}\ , \qquad (52)$$

where $k_{s1,2}$ is the selectivity coefficient with respect to the lightest of the components to be separated in both series, m the difference between the numbers of carbon atoms in the molecules of the last and first component of the first homologous series, and k_{s1} and k_{s2} are the selectivity coefficients for adjacent components of the first and second homologous series. An example of such separation is the analysis of a mixture of straight-chain saturated hydrocarbons and alkylbenzenes on a column with di(β-cyanoethyl) sulphide, where benzene is eluted after nonane. The fraction width Δn, defined as the number of components of the first series which can be separated from the components of the second series, is $\Delta n = m + 1 = 4$. In the examples quoted above with aliphatic acid fractions as stationary phases (Fig. 6) $\Delta n = 1$ for the column with the light fraction and $\Delta n = 2$ for the column with the middle fraction.

b. By using a sorbent of moderate selectivity, characterised by

$$k_{s1,2} \simeq 0.5\, k_{s1} \text{ and } k_{s1} \simeq k_{s2}\ , \qquad (53)$$

i.e. a sorbent which ensures the alternation of the components of both series on elution.

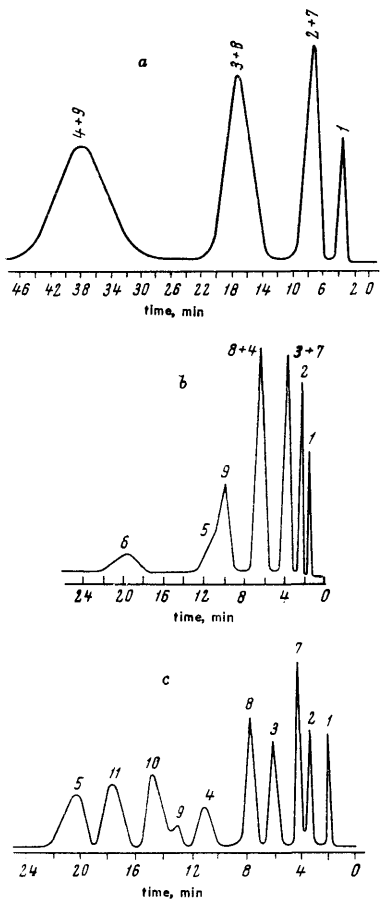


Fig. 6. Chromatograms of mixtures of straight-chain saturated hydrocarbons and alkylbenzenes on columns with different aliphatic acid fractions:
a) light fraction; *b*) middle fraction; *c*) vat residue;
1) hexane; 2) heptane; 3) octane; 4) nonane;
5) decane; 6) undecane; 7) benzene; 8) toluene;
9) ethylbenzene; 10) *m*- and *p*-xylenes; 11) *o*-xylene.

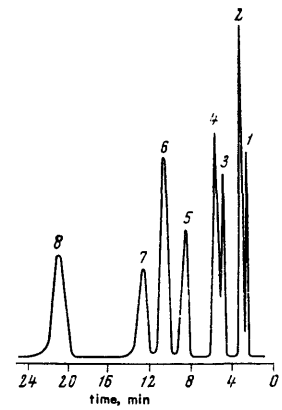


Fig. 7. Chromatogram of hydrocarbons on a column with liquid paraffin:
1) benzene; 2) heptane; 3) toluene; 4) octane;
5) ethylbenzene; 6) nonane; 7) isopropylbenzene; 8) decane.

Relations (53) can hold within wide limits only when the coefficients b_1 and b_2 are identical for both series. Therefore the maximum width of the fraction to be separated should be defined by the formula

$$\Delta n = m + 1 = \frac{0.5\, b_1}{b_2 - b_1} + 1 \quad . \qquad (54)$$

The last condition corresponds to the relation $k_{s1,2} \geq 0.25\, k_{s1}$, i.e. the light component of one series is located midway between two components of the second series and is somewhat displaced towards one of them.

The choice of individual sorbents satisfying the specified conditions is very difficult in many cases, particularly when one deals with the separation not of two but of a large number of homologous series. The search for such sorbents to solve each concrete problem would result in an excessive number of phases used, which is already fairly large. Therefore considerable importance attaches to the use of binary sorbents permitting fine regulation of the selectivity and enabling the peaks on the chromatogram to be displaced relative to one another. A separate section deals with this question.

The procedure involved in the selection of the stationary phase can be significantly simplified by using the relation between the molecular structure of the substance to be separated and its absorption capacity. Recently a number of communications have appeared, dealing with the possibility of calculating the retention volumes assuming additivity, by adding together the increments corresponding to the functional groups[83-87] or different subtypes of the bonds between carbon atoms[88,89]. It is then assumed that

$$\lg V^{rel} = \Sigma n_{ij} A_{ij} \quad , \qquad (55)$$

where n_{ij} is the number of bonds of the given subtype in the molecule of the substance being analysed (or functional groups of the given type) and A_{ij} is the corresponding increment. Eqn. (55) follows from the additivity of the free energy change[90,91], becoming more accurate when a constant term A_0 is introduced on the right-hand side. Special cases of Eqn. (55) are Eqn. (33) and also the method of calculation by the interpolation procedure proposed by Evans and Smith[92].

The authors who calculated retention volumes by the additive procedure used this method only for substances of one class. Indeed when many sorbents are used, the increment per CH_2 group (or bond between secondary carbon atoms) can vary from one homologous series to another. This follows, in particular, from the fact that the $\lg V^{rel}$–n_C lines are not parallel[20,93]. The corresponding lines for various classes of hydrocarbons and their derivatives are parallel only when non-polar solvents are used. Then the method of calculation of retention characteristics by this procedure becomes universal. Evidently the magnitude of the increment is an indication of the selectivity of the phase in relation to the components whose molecules contain the corresponding group or bond[94].

The retention index[75] has significant advantages as a retention characteristic, the additivity of the reduced characteristics entailing the additivity of the index:

$$I = \Sigma n_{ij} B_{ij} + B_0 \quad , \qquad (56)$$

where B_{ij} is the increment per bond (or structural group) and B_0 is a constant.

One of the consequences of Eqn. (56) is the constancy, noted by Evans and Smith[95], within the limits of a homologous series, of the quantity $M_e - M = \Delta M_e$, where M is the molecular weight of the substance and M_e an effective molecular weight equal to the product of the retention index and the sum of the atomic weights of one carbon and two hydrogen atoms (14.026), and also the constancy of "the retention characteristics of the functional group" noted by Swoboda[96].

The difference between the retention indices of two components belonging to different homologous series but containing the same number of carbon atoms in their molecules is a characteristic whereby it is possible to estimate rapidly the suitability of a particular phase for the separation of concrete mixtures. This quantity (δI), which is the difference between the increments per group (or per bond subtype) in the molecules of the series to be separated, is readily tabulated, and does not require a correction for the vapour pressure, which is essential when the factor δ is used. When the coefficients b for homologous series are different, it is necessary to use either average values (as is done in the tabulation of δ values) or values of c and d from Eqn. (57) are tabulated:

$$\delta I = c + d n_C \quad . \qquad (57)$$

The relation between δ and δI is given by equation[97]:

$$\lg \delta + b_T \Delta T_b = b\, \delta I$$

or

$$\lg \delta + b_s \lg \frac{p_1^0}{p_2^0} = b\, \delta I \quad , \qquad (58)$$

where p_1^0 and p_2^0 are the vapour pressures of the substances to be separated, ΔT_b the difference between their boiling points, and b, b_T, and b_s are the coefficients of Eqn. (33).

The difference between the retention indices of a standard substance on squalane and the test phase has also been used as a characteristic of the polarity of the stationary phase[98]. Finally, Rohrschneider[99,100] suggested that the retention indices be calculated from the formula

$$I = I_0 + ax + by + cz + du + es \quad , \qquad (59)$$

where I_0 is the retention index on a column with squalane, a, b, c, d, and e are characteristics of the substance being analysed, and x, y, z, and s are characteristics of the stationary phase.

So far the problem of the selection of stationary phases has been examined only from the standpoint of achieving a definite selectivity without taking into account additional limiting factors, for example the duration of analysis, the column length, the hydraulic resistance of the column[1] etc. It is desirable to select the optimum separation conditions: (a) for a specified accuracy of the analysis (degree of separation of the least readily separated pair of components) on a column of given length with the aim of achieving the fastest possible separation; (b) on a column of given length with the aim of achieving the highest degree of separation; (c) for a specified accuracy with the aim of achieving the most rapid analysis. Therefore, apart from selectivity, it is necessary to consider as the principal properties of the stationary phase its sorption capacity in relation to the most strongly sorbed component and the diffusion characteristics, which are determined by the viscosity.

If the problem is to select a sorbent to attain the most rapid analysis for a specified accuracy on a column of given length, a modified equation for the height equivalent

to the theoretical plate must be resorted to. It can be shown that

$$\frac{H}{L} = A' + B't + C'/t \quad , \tag{60}$$

where H is the height equivalent to the theoretical plate, t the duration of analysis, $A' = A/L$, $B' = B/L^2\Gamma_0$, $C' = C/\Gamma_0$, L is the column length, Γ_0 the overall Henry's constant for the most strongly sorbed component (the ratio of the amount of substance analysed in 1 ml of column volume to its concentration in the gas phase), and A, B, and C are constants of van Deemter's equation[20]. Hence, taking into account Eqn. (2), we have the expression

$$K^2 = \frac{0{,}045\,K_s^2}{A' + B't + C'/t} \quad . \tag{61}$$

Thus the choice of the phase is determined by the specified value of K, the selectivity, and the values of the terms A', B', and C', which depend on the efficiency, column length, and the sorption capacity. Fig. 8 shows different versions of K^2–t plots for two phases under comparison. It is evident that, depending on the specified degree of separation, either one or other phase may be preferable for a more rapid analysis. The time required to separate a two-component mixture for $K = 1$, can be calculated from the relation

$$\frac{t}{K_2} = 22{,}2\,\frac{\Gamma_0 H}{K_s^2 \bar{\alpha}} \quad , \tag{62}$$

where $\bar{\alpha}$ is the average linear flow rate of the carrier gas.

In the analysis of mixtures containing three and more components in the absolute majority of cases the separation factors for neighbouring peaks have different values. Thus, when $K = 1$ is selected for the pair least readily separated, there are "superfluous" sections of the zero line between other pairs corresponding to the excess time expended. The time from the instant of the introduction of the sample to the beginning of the elution of the first peak should be included in this also. If, other conditions being equal, the sorption capacity of the stationary phase is altered in such a way that all the components are separated with equal values of K, the duration of analysis becomes significantly smaller. In other words, on going from a two-component to a multicomponent mixture, the problem of selecting the optimum separation conditions becomes significantly more complex, because a new variable appears, which can be roughly represented by the change of the sorption capacity as a function of the sequential number of the peak on the chromatogram.

The problem of a quantitative estimate of the uniformity of separation was first examined by Peterson and Lundberg[101].

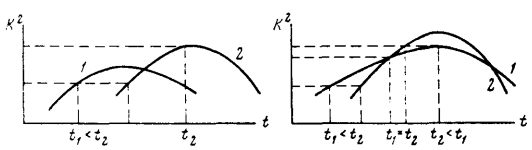


Fig. 8. Various versions on the graphical relation between the degree of separation K and the duration of analysis on a column of specified length with sorbents 1 and 2.

Criteria of the uniformity of separation and the "rapidity" of separation have also been recommended[5,102], whereby it is possible to take into account not only the characteristics determining the separation of two-component mixtures (selectivity, efficiency, sorption capacity) but also those which were previously estimated only qualitatively (uniformity of peak distribution in the chromatogram, desirability of using multistage systems, etc.).

The reduced criterion of uniformity $\bar{\Delta}$ is

$$\bar{\Delta} = \frac{n_k \tau K}{t} \quad , \tag{63}$$

where n_k is the number of peaks, τ the width of the least diffuse peak (in units of time) measured at the height corresponding to the required degree of separation (for example, when almost complete separation is necessary, this is the base of the peak), and K the degree of separation of the pair least readily separated.

The coefficient defining the rate of separation (the "rapid action" coefficient) can be formulated thus:

$$\lambda = \frac{n_k K^2}{t} = \frac{\bar{\Delta} K}{\tau} \quad . \tag{64}$$

The separation of a mixture of C_7–C_{10} straight-chain saturated hydrocarbons on columns containing phases of different polarity [squalane and di(β-cyanoethyl) sulphide] may be examined as an example of the use of λ for the selection of the stationary phase[67]. The corresponding chromatograms and plots of lg V^{rel} against n_C are shown in Fig. 9. The chromatograms were obtained under identical working conditions and for the same efficiency. Evidently best separation on columns of given length is attained with the nonpolar sorbent for which $b = 0.40$ and $k_s = 0.86$ (for the polar sorbent $b = 0.34$ and $k_s = 0.75$). However, if the duration of analysis is the decisive parameter, it is necessary to compare the coefficient defining the rate of separation. Then it was found that the separation of the mixture with the specified degree of separation can be carried out

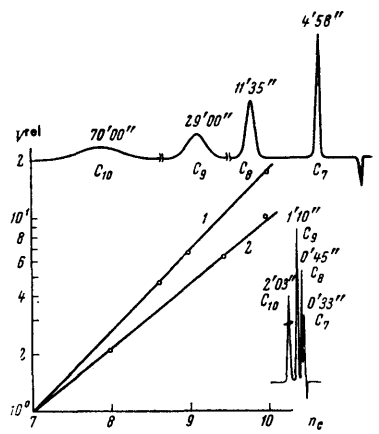


Fig. 9. Variation of the relative retention volumes of straight-chain saturated hydrocarbons with the number of carbon atoms in the molecule; stationary phases:
1) squalane; 2) di(β-cyanoethyl) sulphide; chromatograms obtained on a column 1.2 m long at 60°C and a carrier gas flow rate of 60 ml min^{-1}.

approximately 27 times faster on a column with the non-polar phase, since the "rapid action" coefficient λ is in this case 27 times larger.

If it is necessary to select a phase ensuring the most rapid analysis with a specified accuracy on a column of given length, then the choice depends on the corresponding value of K. If the value of K achieved on the polar phase for the least readily separated pair (heptane–octane) corresponds to the specified value, the polar phase is to be preferred; otherwise the non-polar phase must be chosen.

An estimate of the conditions of chromatographic analysis and, in particular, the suitability of a particular stationary phase for the solution of a concrete problem can be achieved using certain elements of information theory [103]. Thus a method has been proposed [105] on the basis of the concept of useful information [104], whereby it is possible to compare different versions of the analytical procedure. The information defect is the difference between the indeterminacy N_x obtained in the analysis and the entropy S, where

$$N_x = -\sum_{i=1}^{n_k-1} \frac{\psi_i}{\sum_{i=1}^{n_k-1}\psi_i} \mathrm{ld}\,\frac{\psi_{ie}}{\Sigma\psi_{i_e}}$$

and

$$S = \Sigma \frac{\psi_i}{\Sigma\psi_i} \mathrm{ld}\frac{\psi_i}{\Sigma\psi_i} \quad , \qquad (65)$$

ψ_i is the degree of separation of the ith pair of peaks required for the attainment of the specified accuracy, ψ_{ie} the experimental value of ψ, ld denotes a double logarithm, and n_k is the number of peaks. A decrease of the information defect is evidence that the conditions of analysis have become more satisfactory. Instead of ψ one can use other separation factors and also differences between the retention indices of neighbouring components.

6. BINARY SORBENTS

For an optimum separation of complex mixtures, sorbents with a rigorously defined selectivity are required. The problems in the selection of such sorbents can be successfully solved by using binary sorbents of controllable composition. Thus, in the separation of gaseous saturated and unsaturated hydrocarbons a column with a silver nitrate solution is used, but saturated hydrocarbons are eluted as a single peak. On the other hand, a column with the non-polar liquid paraffin does not always lead to a satisfactory separation of ethane from ethylene and of propane from propene, particularly when the detector exhibits significant inertia and the number of theoretical plates in the column is low¶. To achieve a clear separation of all the peaks it is desirable to connect the two columns in series [35].

Columns containing two (or several) individual sorbents can be prepared as follows: (a) sections with individual sorbents are joined in series (compound column); (b) individual stationary liquids are deposited on a solid carrier, the sorbents are mixed, and loaded into the column (column with a mixed sorbent); (c) a mixture of stationary liquids is deposited on a solid carrier (sorbent with a mixed phase).

The dependence of the elution characteristics of substances on columns with binary sorbents on the relative amounts of the individual stationary phases has been investigated by a number of workers [2,35,58,62,106–115]. In those cases where the pressure gradients are low the separation achieved on a compound column is almost identical with that on a column with a mixed sorbent. If the gradients are considerable, they influence the overall sorption characteristics. Thus the effective retention volume [4] of a component on a compound column is

$$V_N = V_{N_1}\frac{j}{j_1}\,\frac{p_{01}}{p_0} + V_{N_2}\frac{j}{j_2} \quad , \qquad (66)$$

where V_{N_1} and V_{N_2} are the effective retention volumes of the component on sections with the first and second sorbent, j the column pressure gradient factor [116], j_1 and j_2 are the pressure gradient factors in the first and second section, p_0 the pressure at the outlet from the column, and p_{01} the pressure at the boundary between the sections. Analogous relations hold also for other retention characteristics [113]. As a result of the influence of pressure gradients, a very interesting effect, first noted by Zhukhovitskii et al., [114] occurs in experiments with compound columns. A change in the sequence of the sections can result in a change of the degree of separation of the components and even in the elution sequence. This effect has been used, in particular, in the development of a method for the determination of the allene and methylacetylene impurities in the propane–propene fraction [117]. Indeed Figs. 10*b* and 10*c* show that with one sequence of the sections the allene and methylacetylene peaks merge into one, which is necessary to obtain a signal to be fed into the control system of the purification process of the propane–propene fraction, while with the reverse sequence the peaks are separated, which is desirable in laboratory analysis.

Graphical relations are used in the selection of the optimum composition of the sorbents; in the general case it is desirable to use for compound columns relations of the type shown in Fig. 10*a*. Here the retention characteristics (reduced retention time, reduced, effective, or specific retention volume) are plotted against the ratio of the reduced lengths of the sections [122], the reduced length of a section being defined thus:

$$L_{\mathrm{red}\,i} = L_i\frac{p_{oi}}{j_i} \qquad (67)$$

where L_i is the length of the section, p_{oi} the pressure at the outlet from the section, and j_i the pressure gradient factor in the given section.

When the effect of the pressure gradient is neglected, the ratio of the true lengths of the sections can be plotted along the abscissa axis. Thus by plotting along the ordinate axis the ratio (t_R/t_0) of the retention time of the given component to that of a non-sorbed substance, Rohrschneider [58] determined the optimum ratio of the lengths of the sections with diethylcyanamide and di(β-cyanoethyl) ether for the analysis of a mixture of C_1–C_5 hydrocarbons.

The corrected peak width on a compound column (ω, ml) can be determined from the following formula:

$$\omega^2 = \omega_1^2\frac{p_{01}^2}{p_0^2}\frac{j^2}{j_1^2} + \omega_2^2\frac{j^2}{j_2^2} \qquad (68)$$

where ω_1 and ω_2 are the corrected peak widths in the first and second sections. Similarly it is possible to calculate

¶ When a high-efficiency column with a non-polar sorbent is used, completely satisfactory, albeit non-uniform, separation of C_1–C_3 hydrocarbons is achieved [102].

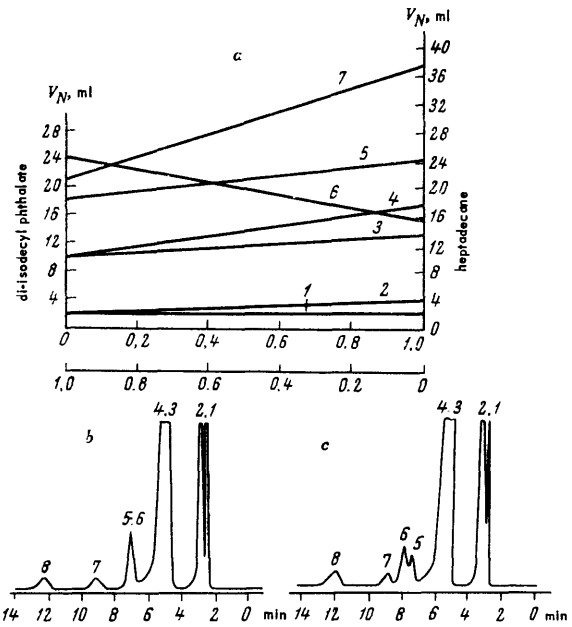


Fig. 10. *a*) Variation of the effective retention volume with the ratio of the effective lengths of sections with heptadecane and di-isodecyl phthalate; chromatograms of the propane–propene fraction on a compound column 7.1 m long;
b) order of sections: 2.4 m with heptadecane and 4.7 m with di-isodecyl phthalate;
c) reverse order; temperature 25°C: 1) ethylene; 2) ethane; 3) propene; 4) propane; 5) allene; 6) methylacetylene; 7) isobutane; 8) n-butane.

the number of theoretical plates, the selectivity coefficient, and the separation factor on compound columns [113]. Thus the degree of separation is defined by the equation:

$$F = \frac{\Delta V_R^2}{\omega_1^2 + \omega_2^2} = \frac{\left(\Delta V_{R_1}^0 \frac{p_{01}j}{p_{0j_1}} + \Delta V_{R_2}^0 \frac{j}{j_2}\right)^2}{\frac{\left(\Delta V_{R_1}^0 \frac{p_{01}j}{p_{0j_1}}\right)^2}{F_1} + \frac{\left(\Delta V_{R_2}^0 \frac{j}{j_2}\right)^2}{F_2}} , \quad (69)$$

where ΔV_R is the difference between the retention volumes of the components on the compound column, ω_1 and ω_2 are the peak widths, $\Delta V_{R_1}^0$ and $\Delta V_{R_2}^0$ are the differences between the corrected retention volumes in the first and second section, and F_1 and F_2 are the separation factors in these sections.

Calculations for columns with mixed sorbents are of course much simpler than for compound columns, because here the optimum ratio of the amounts of the individual sorbents is independent of the pressure gradient. Thus the specific retention volume on a column with a mixed sorbent is

$$V_g = \frac{g_1}{g} V_{g_1} + \frac{g_2}{g} V_{g_2} , \quad (70)$$

where V_{g_1} and V_{g_2} are specific retention volumes (ml g^{-1}) on columns with individual sorbents, $g = g_1 + g_2$, and g_1 and g_2 are the amounts (grammes) of the first and secondary stationary liquid.

The elution characteristics of columns with mixed phases are determined by logarithmic and not linear interpolation. Indeed the following equation follows from the equality of the free energies:

$$\lg V_g = \frac{g_1}{g} \lg V_{g_1} + \frac{g_2}{g} \lg V_{g_2} , \quad (71)$$

This relation is valid only when the excess entropy of the mixture of the two phases is zero [118]. Under the same condition the expression for the retention index is

$$I = I_1 \frac{g_1 b_1}{g_1 b_1 + g_2 b_2} + I_2 \frac{g_2 b_2}{g_1 b_1 + g_2 b_2} , \quad (72)$$

where b_1 and b_2 are the slopes of the plots of $\lg V^{rel}$ against n_C for the first and second phase and I_1 and I_2 are the retention indices on columns with the individual phases.

In conclusion of this section, the work of Porter et al., [119] in which the optimisation of the composition of the mixed phase is achieved with the aid of a computer, may be mentioned.

7. EFFECT OF TEMPERATURE ON THE SELECTIVITY OF THE PHASES; TEMPERATURE LIMITS OF THEIR APPLICATION

Since Henry's constants and also diffusion coefficients depend to a great extent on temperature, the latter is one of the principal factors which determine the duration of analysis, column selectivity, and the degree of spreading of chromatographic zones. Henry's constant (Γ) is known to be exponentially related to the reciprocal of the absolute temperature $1/T$ and therefore an increase of temperature greatly reduces the sorption capacity of the stationary phase.

Fig. 11 shows as an example a plot of the logarithm of the relative retention volume against the reciprocal of temperature† for certain saturated hydrocarbons and cycloalkanes on a column with 12 wt.% of tricresyl phosphate on Chromosorb [120]. Usually, when the temperature is increased, the straight lines corresponding to the individual components approach one another, which leads to a decrease of the selectivity coefficients. This is shown to a particularly high extent when polar forces operate.

However, certain anomalies are also encountered. Thus when a sorbent prepared by solidifying a polyester resin directly on the surface of a solid carrier is used, rapid analysis of a mixture of C_6–C_{10} hydrocarbons can be achieved at 25–30°C. [30] Under these conditions the sorbent exhibits moderate selectivity in the separation of saturated hydrocarbons and alkylbenzenes. When the temperature is raised, the selectivity increases significantly [121]. This is obviously because the sorbent exhibits both adsorption and absorption properties, the latter becoming enhanced at a higher temperature as a result of the decrease of viscosity.

Several papers [122–124] describe chromatographic separation on columns with phases having anisotropic properties and forming liquid crystals in certain temperature ranges. When the temperature is raised above a certain limit, the retention volume decreases sharply, because the phase passes into an isotropic state. The capacity of certain

† A relation of the type of the Antoine equation is more accurate in many cases: $\lg V^{rel} = A + B/(C + T)$, where A, B, and C are constants.

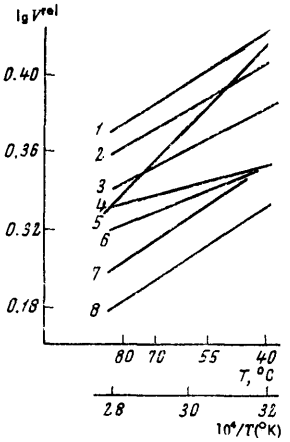


Fig. 11. Variation of the relative retention volume with the operating temperature of a column with tricresyl phosphate: 1) *trans*-1,2-dimethylcyclopentane; 2) *trans*-1,3-dimethylcyclopentane; 3) *cis*-1,3-dimethylcyclopentane; 4) cyclohexane; 5) heptane; 6) 1,1-dimethylcyclopentane; 7) 3-ethylpentane; 8) 2,2,4-trimethylpentane.

substances (in particular *pp*-azoxyphenetole) to form liquid crystals and exhibit selectivity at the same time have been used for the separation of the isomeric xylenes. It is also interesting to note that in many cases it is possible to alter the elution sequence of various substances by altering the temperature. Thus Fig. 11 shows that the position of the heptane peak alters relative to the peaks of the other substances as a function of the operating temperature.

If the values of Γ_S [see Eqn. (14)] for the components being separated are equal, the selectivity coefficient for the column is

$$K_c = \frac{2\varkappa_1\Gamma_S\left(e^{Q_2/RT} - e^{Q_1/RT}\right)}{2\varkappa + \varkappa_1\Gamma_S\left(e^{Q_2/RT} + e^{Q_1/RT}\right)}, \qquad (73)$$

where $\varkappa$ is the fraction of the column volume occupied by the gas phase, $\varkappa_1$ the fraction of the volume occupied by the stationary phase, Q_1 and Q_2 are the heats of solution, and R is the gas constant.

The following relation holds for diffusion in the liquid phase:

$$D_L = D_0 e^{-\beta Q/RT}, \qquad (74)$$

where D_0 is a constant and β the coefficient which can be assumed to be approximately 0.35.[125]

Analysis of theoretical and practical data shows that usually the degree of separation increases as the temperature is reduced, but this involves an increase in the duration of analysis. Evidently it is desirable to reduce simultaneously the operating temperature and the degree of impregnation[126,127], if the overall temperature dependence of the selectivity, sorption capacity, and efficiency indicates an increase of λ.

For a specified duration analysis, there exists an optimum temperature in each system corresponding to the maximum degree of separation. With decrease of the sorption capacity, the optimum temperature falls[82].

The range of operating column temperatures is known to be limited by the requirement that the stationary phase should be almost involatile. But it is recommended that the vapour pressure of the phase at the operating temperature should be not more than 0.5 mmHg (in certain cases a vapour pressure up to 10 mmHg is permitted). The ranges of the operating temperatures for columns with different phases have been tabulated[3,12], their limits being determined not only by the nature of the phase but also by the type of detector and other conditions[129-131]. Since the vapour pressure is related logarithmically to temperature, the "life time" of the column τ_k also decreases logarithmically with temperature. According to Kaiser[9], $\lg \tau_k = k/T$, where k is a constant.

The maximum operating temperature of sorbents with the stationary phases usually employed is such that losses during the first hour of the experiment do not exceed 1% of the total amount of the phase and in the "steady state" they do not exceed 0.1% (the larger losses during the first hour are due to the evolution of volatile impurities)[132]. Only in rare cases are more considerable losses permitted; for example, dimethylformamide, which exhibits high selectivity in the separation of saturated hydrocarbons and olefins, is highly volatile and even at 20°C the losses amount to about 3% per hour.

The method for the determination of the volatility of stationary phases is as follows[132]: 2.0 g of the stationary phase is mixed with 8.0 g of ignited refractory brick and placed in a weighed glass tube. The sorbent layer is compacted somewhat by tapping the tube, after which the tube is reweighed and closed on top by a layer of glass wool. It is then connected to a nitrogen supply and placed in a thermostat set at the required temperature. The flow rate of nitrogen is maintained at 15 ml min^{-1}. After an hour the tube is removed from the thermostat, the nitrogen supply is disconnected, and after being cooled in a desiccator the tube is weighed again. The losses during the first hour and the average losses in the course of the next three hours are recorded.

8. EFFECT OF THE STATIONARY PHASE ON THE SPREADING OF CHROMATOGRAPHIC ZONES

Since the peak width depends both on the sorption characteristic and on the diffusion coefficient in the liquid phase, it is evident that the nature of the stationary liquid phase and its operating conditions have a significant effect on the spreading of the chromatographic zones. Indeed the peak width of the elution curve is related to the width on the sorbent layer σ (cm) by the expression

$$\omega = \Gamma_0\sigma \simeq \Gamma_0\sqrt{LH}, \qquad (75)$$

where Γ_0 is the overall Henry's constant, H the height equivalent to the theoretical plate, and L the column length.

The effect of the stationary phase on the spreading of peaks within the limits of a homologous series has been examined by Turkel'taub[133], who established a linear relation between the logarithm of the peak width and the ratio of the boiling point of the substance to the column temperature. As a result of the proportionality between the peak width and the overall Henry's constant, a linear relation holds between the reduced peak width (the difference between the peak width of the component being analysed and the peak width of a non-sorbable substance) and the number

of carbon atoms in the molecule. This relation obtains also when the column efficiency changes significantly on going from one homologue to another.

If mass transfer by internal diffusion plays a decisive role in zone spreading, the degree of separation is $K' = (\frac{1}{2}\Delta V_R)/\omega_{0.5(1)}$, where ΔV_R is the difference between the retention volumes of adjacent homologues and $\omega_{0.5(1)}$ is the peak half-width of the first homologue, which is related as follows to the number of carbon atoms in the molecule:

$$\lg K' = a' + 0{,}5\, b \cdot n_c \quad . \qquad (76)$$

Here the constant b is the same as in Eqn. (33) and therefore the slope of the $\lg K'-n_C$ line is smaller by a factor of two than the slope of the $\lg V^{rel}-n_C$ line[5].

One of the requirements which must be met by the stationary liquid is that its viscosity should be low. This is quite reasonable when it is remembered that the viscosity is inversely proportional to the diffusion coefficient in the liquid phase. Thus Duffield and Rogers[134] showed that the efficiency of a column with Carbowax 400, whose viscosity is 102 cP (at 25°C), is significantly lower than that of a column with phenylacetonitrile, whose viscosity is 1.98 cP. Quantitative relations characterising the effect of viscosity on efficiency have been given in a number of papers[5,130,135].

If it is assumed that column efficiency is determined solely by internal-diffusion mass transfer, the ratio of the "rapid action" coefficients for two stationary liquids is

$$\frac{\lambda_2}{\lambda_1} = \left(\frac{K_{s2}}{K_{s1}}\right)^2 \left(\frac{\Gamma_{02}}{\Gamma_{01}}\right)^2 \frac{\Gamma_1}{\Gamma_2}\frac{\zeta_1}{\zeta_2}\left(\frac{M_2}{M_1}\right)^{0.5} \frac{\Gamma_{n.1\,(n)}}{\Gamma_{02\,(n)}} \quad , \qquad (77)$$

where the subscripts 1 and 2 refer to the stationary phases, K_s are the selectivity coefficients for the least readily separated pairs, the subscript n refers to the last component, ζ is the dynamic viscosity, and M the molecular weight of the phase. This relation makes it possible to estimate the gain as regards duration of analysis, associated with the selection of a phase having a low viscosity. Examples of the employment of such phases are the rapid analyses on columns with adiponitrile and straight-chain saturated hydrocarbons[5,102].

The data reviewed thus show that, by taking into account the physicochemical characteristics of stationary phases and various relations between them and the retention and spreading parameters, it is possible to solve successfully the problems involved in the selection of the optimum conditions for chromatographic separation.

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STUDY OF MOLECULAR MOTION IN SOLID POLYMERS BY THE INTERNAL FRICTION METHOD

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I. INTRODUCTION

Various properties of solid polymers depend decisively on the nature of the motion of the individual groups and segments of the molecular chains from which they are built up. Therefore it is both of practical and theoretical importance to know the type of molecular motion occurring in the given polymer and the dependence of the type of motion on the composition, structure, molecular weight, temperature, and other factors. One of the most useful physical methods for the investigation of the internal motion of polymeric chains is the internal friction method, the essential features of which are as follows.

When a body is deformed, internal forces (or stresses) arise, due to the change in the distribution of molecules or atoms in it. If the stresses and the relative deformations throughout the period of operation of external forces remain constant and fall to zero instantaneously when the operation of such forces ceases, then we are dealing with a perfectly elastic substance. The isothermal state of such a substance, if the latter is isotropic, is known to be described by the generalised Hooke's law [1]:

$$\sigma_{ik} = 2G\left(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}\right) + K \cdot u_{ll} \cdot \delta_{ik}\,, \qquad (1)$$

where $\dot{u}_{ik} = 0$ when the external forces are constant. Here σ_{ik} is the elastic stress tensor, u_{ik} the deformation tensor, and G and K are the moduli of shear and bulk elasticity respectively.

It is possible also to imagine another ideal case, where the relative deformations of the substance are not constant under the action of constant external forces, but increase continuously at a particular constant rate which is proportional to the stress. The behaviour of such an ideally viscous isotropic material is described [1] by the generalised Newton equation:

$$\sigma'_{ik} = 2\eta\left(\dot{u}_{ik} + \frac{1}{3}\delta_{ik}\dot{u}_{ll}\right) + \zeta\dot{u}_{ll} \cdot \delta_{ik}\,, \qquad (2)$$

where σ'_{ik} is the dissipative stress tensor, $\dot{u}_{ik}$ the derivative of the deformation tensor with respect to time, and η and ζ are the shear and bulk viscosities.

However, in no real substance with a definite structure can stresses exist indefinitely or decrease instantaneously, since during deformation the structure of the substance changes continuously (and in a complex manner) at a certain finite velocity, determined by the nature of the substance. Therefore the behaviour of a real material is in fact described by more complex relations than Eqns. (1) and (2).

The nature of these relations is most readily elucidated using the state of idealised linear stress as an example. Since shear deformations are of the greatest importance in mechanical problems associated with polymers and plastics, we shall consider homogeneous shear deformation. For this case,

$$u = u_y \text{ and } u_{yz} = \frac{1}{2}\frac{\partial u_y}{\partial z} .$$

For non-zero components of the stress tensor, we find from Eqns. (1) and (2)

$$\sigma_{yz} = G\frac{\partial u_y}{\partial z},\ \sigma'_{yz} = \eta\frac{\partial u_y}{\partial z} . \qquad (3)$$

The behaviour of an ideally viscous material described by Newton's equation [Eqn. (3)] can be represented schematically by a section of a $\partial\dot{u}_y/\partial z - \sigma_{yz}$ straight line passing through the coordinate origin (Fig. 1, curve I). The direct proportionality of the flow rate gradient $\partial\dot{u}_y/\partial z$ to the stress σ_{yz} implies that the shape and state of the structural elements of the object do not undergo any changes and that the shear stress increases and decreases instantaneously.

The flow of high polymers and plastics does not usually[2] obey Newton's equation [Eqn. (3)]. Their flow rate gradient can increase with shear stress either faster (Fig. 1, curve II) or more slowly (Fig. 1, curve III). Apart from fluidity, polymers and plastics exhibit a certain elasticity and therefore the onset of non-elastic deformation (flow) does not as a rule coincide with the origin of the coordinates (Fig. 1, curves IV–VI) of the $\partial\dot{u}_y/\partial z - \sigma_{yz}$ curve. Therefore the total deformation in a solid under the influence of a mechanical load can be represented by the sum of two terms: the reversible† (elastic) deformation u'_y propagated at the velocity of sound and the irreversible (plastic) deformation u''_y. The latter type of deformation in a real substance is not established instantaneously but increases gradually when an external constant load is applied. Its experimental time dependence $u''_y = \Phi(t)$ is very complex and is related to the previous history of the specimen. As a result, when the external load is changed periodically there is a phase lag between the total deformation and the stress, which entails energy dissipation by vibrations. The capacity of a substance to transform the energy of mechanical vibrations into heat is known as mechanical losses or internal friction‡. The following quantity can serve as a measure of internal friction:

$$\delta = \Delta E/E , \qquad (4)$$

where ΔE is the energy dissipated during the cycle and E the vibrational energy. The physical cause of internal friction is the rearrangement in the solid occurring at a finite rate under the influence of mechanical stresses. Five types of this kind of rearrangement are known: thermal rearrangement (thermoelastic effects), electrical rearrangement (electron redistribution, ion migration, rotation of electrical dipoles, and other effects), magnetic rearrangement (magnetomechanical hysteresis, relaxation of the magnetic flux as a result of the appearance of macro- or micro-fluxes, rotation of magnetic dipoles, and other effects), atomic rearrangement (ordering of the atoms under the influence of the stress, the appearance, redistribution, and migration of dislocations, etc.), and molecular rearrangement (relative displacement of groups, segments, and the entire molecules).

In the present review special attention is given mainly to the last type of rearrangement which has been least investigated§. The first four types of internal rearrangement and the mechanisms of internal friction associated with them have been fairly thoroughly examined at various times by numerous investigators (see the review articles [7–11]).

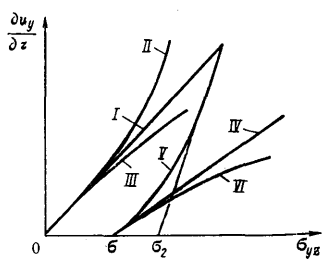


Fig. 1. Principal types of flow curves: I) viscous Newton substance; II) and III) "quasi-viscous" substance; IV) Bingham's "plastic" substance; V) and VI) "quasi-plastic" substance; σ_2—conventional limit of fluidity.

† If the substance exhibits rubberlike elasticity, it is essential to take into account also the rubberlike deformation.

II. METHODS OF MEASUREMENT OF INTERNAL FRICTION

Internal friction can be measured by different methods: (1) from the temperature variation of the substance during deformation; (2) from the variation of the phase shift angle between the stress and the deformation; (3) from the amplitudes of free and forced vibrations at various frequencies; (4) from the decay of elastic waves. The first [12,13] and the second [14–16] methods have not been widely used. The third and fourth methods are the most extensively applied and therefore we shall in fact consider them, leaving aside methods developed for rubberlike materials (see, for example, the review by Bartenev et al. [17]).

1. Methods of Free and Forced Vibrations

The third group of methods is usually divided into two parts. The first part includes all the low-frequency methods and the second all the high-frequency methods. We shall consider briefly the methods in each subsection of this group separately.

a. Low-frequency methods. The low-frequency methods include all known methods based on torsional, bending, longitudinal, and transverse vibrations in the range between 10^{-3} and 10^2 c/s. At vibration frequencies above 2 c/s the variation of the amplitude with vibration frequency is usually recorded automatically. At lower frequencies it is possible (and very convenient) to make visual observations.

‡ In earlier studies [3] internal friction was erroneously identified with the viscosity.

§ It has been partially described by Kolsky [4] and Ferry [5]. Molecular motion in polymers has been described by Mikhailov and Borisova [6].

The oldest and the simplest of all the low-frequency methods for the measurement of internal friction is that of the torsional pendulum. As early as 1837, Weber[18] used the torsional pendulum to solve the problem of the non-elastic behaviour of silk threads, whereby he initiated the studies of internal friction by this method. The torsional pendulum method received general recognition in subsequent years. The method has been used particularly extensively during recent years after its very successful application[19-21] in the study of the viscous behaviour of grain boundaries in metals.

The principal disadvantages of the method of low-amplitude torsional vibrations, which otherwise has many advantages[21], are the inhomogeneity of the deformation of the specimen (the relative amplitude of deformation varies from a maximum of 10^{-5}–10^{-4} on the surface of the specimen to zero at its axis) and the presence of a constant extensive load due to the weight (of the order of 30–50 g) of the inertial system attached to the lower end of the specimen. A torsional pendulum free of the last defect was proposed in 1954 by Ang and Wert[22] and in the same year by Jenckel[23]. It is known as the "reversible torsional pendulum". Its most successful version was developed and constructed in 1960 by Piguzov[24]. This apparatus permits the measurement of internal friction and the modulus of shear in the temperature range between 80° and 770°K. In its design provision is made for the irradiation of the specimen with ultraviolet and X-rays and for the deformation of the specimen directly during the measurement.

Other versions of the torsional pendulum with different design features are also known[25-31]. A novel apparatus, permitting the measurements of the internal friction in polymers and plastics in the frequency range between 10^{-3} and 10^{2} c/s during bending vibrations has been described by Maxwell[33] and apparatus for the measurement of internal friction during torsional vibrations in the infrared frequency range has been described by Illers and Breuer[34] (see also Refs. 35 and 36). Illers[35] described a novel method for the measurement of mechanical losses at a frequency of about 1 c/s.

A simple shear pendulum has been proposed by Rorden and Grieco[37]. Methods in which longitudinal vibrations are used[38,39] have been developed predominantly for materials with rubberlike elasticity. A very interesting method, for materials of the same type, using longitudinal vibrations excited electrically has been described by Hutton and Nolle[40]. The logarithmic decay decrement θ, or the quantity Q^{-1}, which is smaller by a factor of π, serve as measures of the internal friction in this method. The last symbol was introduced by analogy with the decay of electromagnetic oscillations in electrical circuits[9]; Q is the Q-factor of the system in which the mechanical vibrations are excited.

We may note that materials with a very small internal friction (of the order of 10^{-5}) cannot be investigated with the aid of a torsional pendulum (of whatever design), for example, since under these conditions the decay resulting from the losses in the apparatus has an effect.

b. High-frequency methods. These methods are characterised by the absence of a special inertial system linked with the specimen. The specimen in the form of a rod executes torsional, longitudinal, transverse, or bending vibrations at one of its natural frequencies. Steady forced vibrations (resonance method) and the decay of natural vibrations (the method of free vibrations) can be used for the measurements. In the first case the internal friction is measured by the quantity

$$B=\frac{\Delta\nu}{\nu_0}\ , \qquad (5)$$

where $\Delta\nu$ is the half-width of the resonance peak. In the second method the internal friction is measured, as in the low-frequency methods, by the logarithmic decay decrement θ or Q^{-1}.

The frequency range depends on the type of vibrations excited and the size and shape of the specimens. For example, in torsional, longitudinal, and transverse vibrations the frequency is usually between about 10^2 and 10^6 c/s. In bending vibrations the frequency is in the range approx. 10^2–10^4 c/s.

High-frequency vibrations can be excited and recorded in different ways. However, most investigators use the same methods for both purposes. Depending on the way in which the forced vibrations are excited, all the high-frequency methods can be divided into electrical, piezoelectric, electromechanical, and electromagnetic.

In the electrostatic method (Fig. 2*a*) mechanical vibrations are excited by applying an alternating potential to a condenser, one plate of which is the end of the specimen (covered by a conducting layer in the case of polymer) and the end is a stationary plate. To record the vibrations, it is possible to use the same type of condenser at the other end of the specimen, operating as a capacitive microphone. The electrical method is suitable for longitudinal, bending, and torsional vibrations. The method was used for the first time by Bancroft and Jacobs[41] to excite longitudinal and bending vibrations in metallic rods. It was then used by Parfitt[42] for polymers. A description of the subsequent use and development of this method can be found in Refs. 14, 43–49, etc.

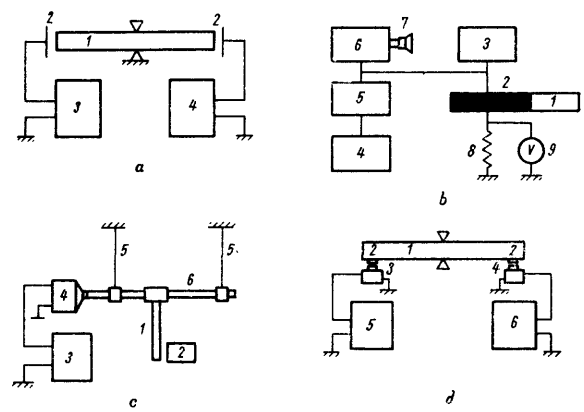


Fig. 2. Schematic representation of high-frequency methods for the measurement of internal friction:
a): 1) specimen; 2) condenser plates; 3) oscillator; 4) detector;
b): 1) specimen; 2) quartz; 3) constant amplitude and alternating frequency generator; 4) constant frequency generator; 5) multivibrator; 6) amplifier; 7) reproducer (beat detector); 8) resistance; 9) valve voltmeter;
c): 1) specimen; 2) "detector"; 3) oscillator; 4) electromechanical transducer; 5) flat springs; 6) connecting rod;
d): 1) specimen; 2) pole pieces; 3) and 4) electromagnetic transducer and receiver; 5) oscillator; 6) detector.

In the piezoelectric method (Fig. 2*b*) the specimen of the test material in the form of a rod is attached by a cement to the end-face of the piezo-quartz rod. When an alternating potential is applied to the piezo-quartz rod, the specimen and the quartz begin to vibrate as a single body (compound vibrator), executing longitudinal or torsional vibrations. From the variation of the current flowing through the quartz, measured by means of a valve voltmeter *9* (or determined from the changes in the resonance curve), it is possible to determine the internal damping of the system, which yields the overall internal friction of quartz and the specimen. The internal friction of quartz can be determined separately and allowed for. The vibration frequencies of the compound vibrator are measured by the method of beats.

Quimby[50,51] and then Zacharias[52] were the first to use this method to measure the internal friction in solids. The compound vibrator method has been applied to the investigation of polymers in Refs. 53–56 and other investigatons. It has been found[57] that, as a resutl of the differences between the coefficients of linear expansion of quartz and the specimen, the internal friction is greatly influenced by the deformations in the cementing layer. This effect is small if the specimen and the quartz rod are selected to ensure that they have similar natural vibrations so that a vibration node is located at the point of attachment. This requirement cannot always be satisfied and therefore the method is not suitable for the investigation of internal friction as a function of temperature. Using a number of precautions, Mikhailov and Solov'ev[54,56] and Wada and Yamamoto[55] nevertheless succeeded in investigating the temperature vibration (in the range between 100° and 360°K) of the internal friction of certain polymers by the compound vibrator method.

In the electromechanical method the vibrations of the specimen are excited by an electromechanical transducer of special design[14,58,59] or simply with the aid of a loudspeaker[60,61], as shown in Fig. 2*c*. In the earliest studies[60,62] the amplitude of the vibrations of the specimen was measured visually using a microscope.

A photoelectric method has been employed for recording the vibrations of specimens[14,58]. Robinson's work[58] is particularly interesting, since he developed a method whereby it is possible to measure the internal friction in the temperature range between 20° and 600°K at vibration frequencies between 10^2 and 10^3 c/s.

Capacitive and inductive methods have been employed for the recording of vibrations[63,64]. An improved capacitive method has also been described[61] for the measurement of the vibration amplitudes in the frequency range between 6 and 6000 c/s. The temperature during the measurements could vary between −50° and +300°C.

In the electromagnetic method (Fig. 2*d*) a disc of a ferromagnetic material is attached to each end of the specimen by means of a special cement. A coil (supplied with power from an oscillator) located near one of the ends of the specimen sets up an alternating magnetic field which interacts with the ferromagnetic disc and gives rise to the vibration of the specimen. In a second coil (near the second disc) an e.m.f. is induced and then amplified and recorded. The relative positions of the coils and discs determine the type of vibration: depending on the relative positions, the vibrations can be longitudinal[65,66], bending[22,67,68], and torsional[69]. The method is not very suitable for the measurement of low internal frictions, since the discs can move at their points of attachment causing additional energy losses. Forster[70] eliminated this defect by modifying the method. In his procedure the vibrations of the specimen are transmitted via a wire suspension. They are then transmitted through another wire suspension to the recording device. This method is suitable for the measurement of internal friction at high temperatures: the wires emerge from the furnace and the entire electrical section is at room temperature. After some design modifications; Kline[71] used Forster's method to investigate the internal friction in polymers at temperatures between 4° and 600°K and frequencies between 50 and 5000 c/s.

Borovitskaya[72] used an optical interference-modulation method[73] to investigate the internal friction in rubberlike materials at frequencies between 10^2 and 10^5 c/s.

2. Method of Wave Propagation

This method for the investigation of internal friction consists in the measurement of the decay of the stress wave during its propagation in the solid. Under certain conditions[4] it is possible to compare this decay with the internal friction determined by the methods examined above. It can be shown that the absorption coefficient α and the quantity δ are related to the wavelength λ as follows:

$$\alpha = \frac{1}{2\lambda}\delta \ . \qquad (6)$$

Using the case where only one relaxation process, characterised by one relaxation time τ, takes place in the solid, Zener[74,75] showed that the parameters (examined above) defining internal friction are simply related¶, regardless of the exact mechanism of energy dissipation, provided that the internal friction is low (for example, $\tan\varphi \leqslant 0.1$). This relation is as follows:

$$\tan\varphi = \frac{\theta}{\pi} = \frac{\delta}{2\pi} = \frac{B}{\sqrt{3}} = \frac{\lambda}{\pi}\frac{\alpha}{\pi} \ . \qquad (7)$$

Bearing in mind the above relation, it is possible to express the absorption coefficient in terms of any parameter used as a measure of internal friction. However, one must not forget that in fact the decay of the pulse is not due solely to absorption but also to a large extent to dissipation at inhomogeneities. The decay of the stress waves is particularly pronounced when the average size of an individual inhomogeneity is comparable to the wavelength. Under these conditions the decay of stress waves is caused not so much by absorption, whose mechanism is similar to that of internal friction, as by diffusive scattering of stress waves by the inhomogeneities.

The method of wave propagation can be subdivided into two separate procedures: the method of "travelling waves" and the pulse method. The method of travelling waves was first used by Ballow and Silverman[79] and then by Nolle[80],

¶ Eqn. (7) breaks down when $\tan\varphi > 0.1$; it depends on the mechanism of energy dissipation[76]. In the region of very high internal friction the logarithmic decay decrement cannot serve as a reliable characteristic and in the region of aperiodic motion the concept of a logarithmic decrement loses all significance. Therefore in the aperiodic region and in the adjacent regions (see Figs. 7, 8, and 10) of rapid decay of the vibrations, it is necessary to use other quantities as characteristics of internal friction, for example the absorption coefficient[77] α or the coefficient of mechanical losses, which in this case is related to $\tan\delta$ in a different way[78].

Kuznetsov[81], and others. The theory of this method and the calculation of the dynamic characteristics of the material have been discussed[82-84]. The method has been developed most completely (Fig. 3*a*) by Volodin[85].

This method for the measurement of α can be used only in a restricted frequency range (approx. 10^3-10^5 c/s) and for materials with values of α which are neither unduly large nor unduly small[81,85].

The pulse method (Fig. 3*b*) consists in the excitation of a short high-frequency vibration pulse ($\nu \simeq 10^5-5\times10^8$ c/s) and the measurement of its propagation and decay times during passage through the specimen. In the earliest studies[86-88] the pulses lasted between 1 and 15 μs with vibration frequencies of the order of 10^8 c/s. The pulse passes back and forth through a liquid (transmitting medium) and along the specimen *1* and is detected by the receiving crystal *3*. The relative amplitudes of the successive pulses determined with a valve voltmeter *8* provide a measure of the decay and the time intervals between them, determined by an oscilloscope *7*, give the rate of propagation.

The method was developed further by other workers[89-94]. In their study of the intrinsic piezo-effect of quartz, Merkulov and Yakovlev[94] measured the absorption coefficient of quartz (for shear and longitudinal waves) by the pulse method up to hypersonic frequencies ($\nu \simeq 10^9$) in the temperature range between −200° and +200°C.

As shown above, the results obtained by the pulse method must be interpreted with some caution. It is necessary to take into account the "spreading" of the pulse during its propagation in the absorbing medium (due to the dispersion of the velocity of sound) and also the fact that the overall weakening of the pulse is due not only to absorption but also to a large extent to scatter by inhomogeneities.

A pulse method for hypersonic frequencies (approx. 10^9-10^{10} c/s) has been described[95,96]. This method, which is a development of Baranskii's method[97], is based on hypersonic excitation in a quartz rod with the aid of an electromagnetic cavity resonator. The quartz rod is the test specimen. Hypersonic vibrations of higher frequencies ($\nu \simeq 10^{12}-10^{13}$ c/s) cannot be excited artificially. We may note that the limit of natural thermal hypersonic frequencies is of the order of $10^{12}-10^{13}$ c/s even in crystalline materials. The study of the rate of propagation and absorption of natural hypersonic vibrations in crystals is possible only by indirect methods, namely optical[98] and X-ray[99-103] methods.

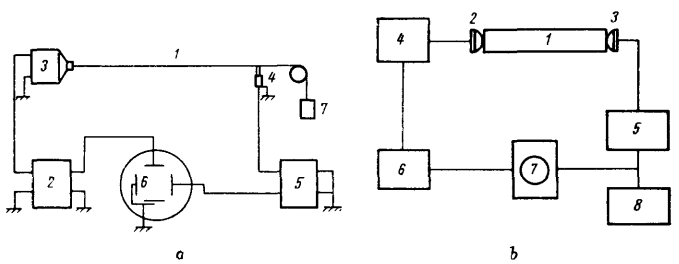


Fig. 3. Schematic representation of the "travelling wave" and pulse methods for the measurement of the rates of propagation and absorption of vibrations in solids:
a): 1) threadlike specimen; 2) oscillator; 3) electromechanical transducer; 4) piezoelectric rod; 5) amplifier; 6) double-beam oscilloscope;
b): 1) specimen; 2) piezoelectric transducer; 3) piezoelectric receiver; 4) pulse generator; 5) amplifier; 6) synchronisation unit; 7) oscilloscope; 8) valve voltmeter.

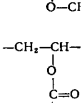
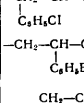
III. EXPERIMENTAL RESULTS

The solid polymers and plastics which have been investigated are listed in the Table which indicates the range of conditions investigated, the method of investigation, and the literature sources available to the author of the review. It is evident from the Table that technically important polymers such as polyethylene, polystyrene, poly(vinyl chloride), polyamides, and acrylic acid polymers have been most completely investigated. Few studies have been made on plastics.

TABLE.

No.	Polymer	Monomer unit	Range investigated: temperature, °K	Range investigated: frequency, c/s	Method	Refs.
1	polyethylene	$-CH_2-CH_2-$	110—400	~1	torsional vibrations	104—108
			85—400	~1	shear vibrations	109
			80—450	10^2-10^3	transverse vibrations	110—116
			50—550	10^2-10^3	ditto	117,118
			170—350	10^2-10^3	»	119
			300—425	10^2-10^3	shear vibrations	120,121
			190—425	10^3-10^4	longitudinal vibrations	14,49, 122—127
			110—370	10^4-10^5	ditto	128—130
			210—340	~10^6	shear waves	128—130
			275—360	~10^6	longitudinal waves	55,92,128, 130,131
2	polyoxymethylene	$-CH_2O-CH_2O-$	100—450	~1	torsional vibrations	132—134
3	poly-α-olefins	$-CH_2-CH-$ (R)	80—350	10^2-10^3	transverse vibrations	135
4	polypropylene	$-CH_2-CH-$ (CH_3)	50—450	10^2-10^3	transverse vibrations	136
			190—275		longitudinal vibrations	49
			230—400		longitudinal waves	137
5	polyisobutylene	$-CH_2-C-$ (CH_3, CH_3)	110—415	~1	torsional vibrations	104
			300	$30-5\cdot10^3$	shear vibrations	138
			230—375	10^2-10^3	ditto	139
			290	~10^6	longitudinal waves	92
6	poly(vinyl chloride)	$-CH_2-CH-$ (Cl)	~300	$10^{-3}-10^2$	Lending vibrations	33
			125—425	1—10	torsional vibrations	27,60,101, 140
			25—350	10^2-10^3	transverse vibrations	111
			255—300	10^2-10^3	shear vibrations	138
			285—375	10^6	longitudinal waves	55,92,141
			175—475	10^6	ditto	142
7	poly(vinylidene chloride)	$-CH_2-C-$ (Cl, Cl)	110—470	~1	torsional vibrations	104
8	poly(vinyl alcohol)	$-CH_2-CH-$ (HO)	175—475	~1	torsional vibrations	142
			290—450	10^2-10^3	transverse vibrations	143
9	polyacrylonitrile	$-CH_2-CH-$ ($C\equiv N$)	110—500	~1	torsional vibrations	104
10	polystyrene	$-CH_2-CH-$ (C_6H_5)	100—210	~1	torsional vibrations	144
			135—425	~1	ditto	23,104,107 145,146
			50—500	10^2-10^3	transverse vibrations	61,110,111, 147,148
			50—300	10^3-10^4	longitudinal vibrations	49,149,150
			210—365	10^4-10^5	ditto	125,127
			290	10^6	»	92
			175—475	10^6	»	142
			210—370	10^6	»	58
11	polyvinylstyrene	$-CH_2=CH$ / CH_2-CH- (C_6H_5)	~300	10^2-10^3	shear vibrations	129
12	poly(methyl acrylate)	$-CH_2-CH-$ ($CH_3O-C=O$)	~315	$10^{-1}-10^3$	torsional and transverse vibrations	151

TABLE (contd.)

No.	Polymer	Monomer unit	Range investigated: temperature, °K	Range investigated: frequency, c/s	Method	Refs.
13	poly(methyl α-chloroacrylate)		220—430	10^2—10^3	transverse vibrations	152
14	poly(methyl methacrylate)		250—350	10^{-3}—10^2	bending vibrations	153
			30—300	10^3—10^4	ditto	154
			150—435	~1	torsional vibrations	155,156
			4.2—100	~1	ditto	157
			190—400	1—10^2	»	28,158-160
			200—400	10^2—10^3	transverse vibrations	28,158,160
			290—370	10^2—10^3	longitudinal vibrations	48
			225—385	10^3—10^4	ditto	49
			225—355	10^4—10^5	»	125
			290—380	~10^6	longitudinal waves	55,92,161, 162
15	poly(ethyl methacrylate)		4.2—100	~1	torsional vibrations	157
			225—285	~1	ditto	151
			~315	10^{-1}—10^3	torsional and transverse vibrations	151
16	poly(cyclohexyl methacrylate)		~315	10^{-1}—10^3	torsional and transverse vibrations	151
17	poly(methyl α-cyanoacrylate)		220—430	10^2—10^3	transverse vibrations	152
18	poly(tributyl methacrylate)		~315	10^{-1}—10^3	torsional and transverse vibrations	151
19	poly(isobutyl vinyl ether)		110—370	1—10	torsional vibrations	104,163
20	poly(vinyl acetate)		125—460	$2 \cdot 10^6$	longitudinal waves	164
21	poly-p-chlorostyrene		100—210	10^{-1}—1	torsional vibrations	144
22	poly-p-bromostyrene		100—210	10^{-1}—1	torsional vibrations	144
23	polyvinyl carbazole		120—525	~1	torsional vibrations	104,163
24	polybutylene		240—285	10^3—10^4	longitudinal vibrations	49
25	polytetrafluoroethylene		125—435	~1	torsional vibrations	155,165
			20—560	~1	ditto	30,31,106, 163,166
			4.2—100	~1	transverse vibrations	111,112
			50—600	10^2—10^3	shear vibrations	120
			300	10^2—10^3		
26	polychlorotrifluoroethylene		150—500	~1	torsional vibrations	158
			110—470	~1	ditto	104,163
27	phenol formaldehyde resins		200—360	10^3—10^4	longitudinal vibrations	49
			200—450	10^4—10^5	ditto	125,127
			290—360	10^6	»	55
28	poly(di-o-cresyl carbonate)		100—510	~1	torsional vibrations	167
29	polyester resins	polymer of complex structure	220—520	~1	torsional vibrations	104,163
			240—360	10^4—10^5	longitudinal vibrations	
30	polyamides	ditto	100—485	~1	torsional vibrations	168,169
			110—525	~1	ditto	104,106
			50—600	10^2—10^3	transverse vibrations	111,170,171
			235—535	10^3—10^4	longitudinal vibrations	49
			210—290	10^4—10^5	ditto	125
			265—335	10^6	longitudinal and shear waves	128
			290—360	10^6	longitudinal waves	55
31	polyesters	»	210—525	~1	torsional vibrations	27
32	polyurethanes	»	101—425	~1	torsional vibrations	23,106, 172—174
33	celluloid	plastic	200—450	~1	torsional vibrations	27
			300	10^3—10^2	bending vibrations	33
			290—360	10^6	longitudinal waves	55
34	ebonite	ditto	290—450	10^2—10^3	transverse vibrations	175
			290—360	~10^6	longitudinal waves	53,55
35	Novolak plastics	»	290—700	~1	torsional vibrations	21

We shall consider briefly the principal results of studies on the temperature and frequency dependence† of the internal friction in polymers and plastics on various factors: structure, impurity content, thermal and mechanical treatment, irradiation, etc., using as examples the macromolecular compounds which are technically the most important.

1. Temperature Dependence

Figs. 4*a*, 4*b*, and 5 show the temperature variation of the internal friction of polyethylene, polystyrene, and poly(methyl methacrylate) of technical purity at various frequencies. The results demonstrate that the Q^{-1}–T curves for all the polymers examined have one or several maxima whose positions along the temperature axis may depend on the vibration frequency (as can be seen in Fig. 5). Fig. 5 shows that, with increasing frequency, the internal friction peak is displaced towards higher temperatures, degenerates into a point of inflection, and finally disappears altogether. However, the peaks on the polyethylene Q^{-1}–T curve, for example, do not disappear when the frequency is increased from 1 to 10^6 c/s and their position along the temperature axis changes little, although their shape does alter appreciably. The shape is very sensitive to the number of methyl groups in the polyethylene macromolecule [117].

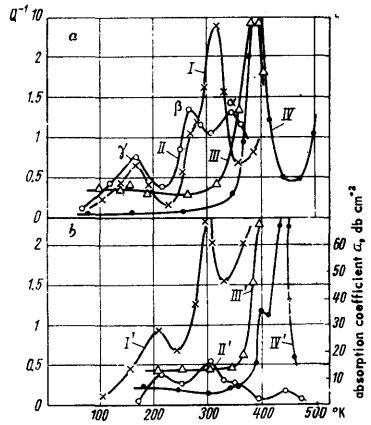
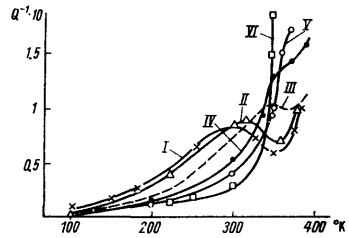


Fig. 4. Temperature variation of the internal friction and of the absorption coefficient α of polyethylene (curves I and II) and polystyrene (curves III and IV):
a) frequencies: 1 c/s for curves I and III and about 10^3 c/s for curves II and IV;
b) frequencies: about 10^4 c/s for curves I and II and about 2×10^6 c/s for curves III and IV.

† For low deformation amplitudes, which usually obtain in measurements of internal friction, the variation of internal friction with the experimental temperature and vibration frequencies is of fundamental importance (see the theory). Various factors (preceding treatment, impurities, irradiation, etc.) alter $Q^{-1}(T)$ and $Q^{-1}(\nu)$. By studying these changes, we are able to assess the nature of molecular motion in solid polymers.



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Fig. 5. Temperature and frequency dependence of the internal friction of poly(methyl methacrylate);[49,158] frequency (ν, c/s):
I) 0.4; II) 2; III) 20; IV) 200; V) 2×10^3;
VI) 3×10^4.

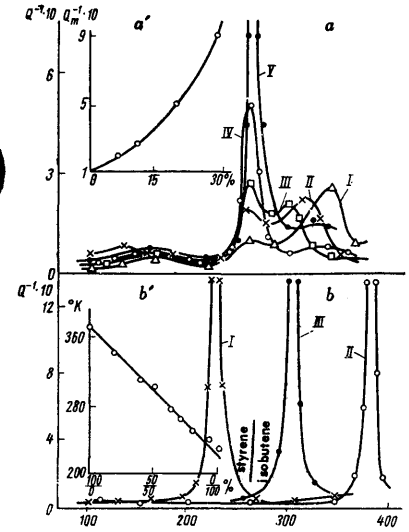


Fig. 6. Effect of chlorine on the shape of the $Q^{-1}-T$ curve for polyethylene:
a) frequency $\nu \sim 1$ c/s:[104] I) 0 wt.% Cl; II) 5.8 wt.% Cl; III) 10.4 wt.% Cl; IV) 12.3 wt.% Cl; V) 28.2 wt.% Cl;
a') variation of the height of the 270°K peak on the $Q^{-1}-T$ curve with the chlorine content;
b) temperature variation of the internal friction of a mixture of polyisobutylene and polystyrene at $\nu \sim 1$ c/s:[104]
I) polyisobutylene; II) polystyrene; III) 50% polystyrene–50% polyisobutylene mixture;
b') temperature variation of the Q_m^{-1} maximum with the ratio of styrene and isobutene in the mixture.

The shape of the peaks depends significantly also on other factors, in the first place on the relative amounts of the amorphous and crystalline phases in the solid polymer. Thus the low-temperature peak on the $Q^{-1}-T$ curve for Teflon decreases in height with increasing degree of crystallinity, while the height of the peak in the region of 300°K actually increases with increasing crystallinity[31,165]. The high-temperature peak on the Teflon $Q^{-1}-T$ curve (at about 400°K) varies with the degree of crystallinity in a more complex manner.

Another factor which influences significantly the shape of the peak is impurities. Fig. 6*a* shows this effect in polyethylene containing various amounts of chlorine atoms. It is seen that for technically pure polyethylene there is a point of inflection near 270°K instead of the peak. With increasing percentage content of chlorine atoms in polyethylene, the peak not only becomes distinct but also increases rapidly in height (Fig. 6*a'*). The high-temperature peak (340°K) also varies appreciably on introduction of chlorine atoms into polyethylene but the variation of its height and position is more complex. The effect of chlorine atoms on the position and height of the low-temperature peak (at about 170°K) is slight.

The position of the maximum in the $Q^{-1}-T$ curve can also depend on the molecular weight of the polymer. For example, increase of the molecular weight of polystyrene[104] from 80 000 to 120 000 causes a displacement of the peak (without significant change in its height) towards higher temperatures by about 16 deg, but effects of this kind are not always observed. For example, a change of the molecular weight of polyisobutylene from 500 000 to 1 750 000 changes neither the position nor the height of the peak on the curve[104].

According to Fig. 6*b*, the $Q^{-1}-T$ curves for polyisobutylene and polystyrene have distinct maxima. A mixture‡ of these polymers also gives rise to a peak (Fig. 6*b*, curve III) on the $Q^{-1}-T$ curve, whose position on the temperature axis (Fig. 6*b'*) depends on the relative amounts of styrene and isobutene in the mixture.

It has been shown[104] that heat treatment influences the form of the $Q^{-1}-T$ curve for a mixture of poly(vinyl chloride) and poly(vinylidene chloride). In the first place the authors draw attention to the fact that, in contrast to pure amorphous polymers which have no peaks on the $Q^{-1}-T$ curve, the curve for a mixture of amorphous homogeneous polymers has an internal friction peak at approximately 300°K. Crystallisation of the mixture (as a result of the heat treatment) leads to the appearance of a second peak on the $Q^{-1}-T$ curve, whose height increases slightly with increasing amount of the crystalline phase, while the peak characteristic of the amorphous phase decreases sharply.

Irradiation has a significant effect on the shape of the $Q^{-1}-T$ curve. Irradiation with γ-rays emitted in the decomposition of radioactive cobalt-60 nuclei at a selected dose (about 100 mr) does not give rise to an appreciable change[111] of the shape of the $Q^{-1}-T$ curve for non-irradiated polyethylene. The situation changes markedly when polyethylene is irradiated with a neutron beam of the order of 10^{18} neutron cm^{-2} s^{-1}.[111,115,118] With increasing intensity of the neutron beam, the low-temperature γ-peak initially broadens and increases in height and then begins to be displaced towards higher temperatures with a simultaneous decrease in height. At the same time the β and α peaks merge into a single, broad peak, which then vanishes altogether.

Summarising, one may say that the $Q^{-1}-T$ curve characterises a given polymer under concrete conditions. Each change in the specimen, be it a change in molecular weight, composition, degree of crystallinity, etc., is reflected in

‡ For more detailed information on the composition of the polymers see, for example, Bartenev et al.[35]

a characteristic change in the shape of the internal friction–temperature curve. We shall see below that theoretical and experimental studies of these changes provide information about the characteristic features of the mechanism of certain processes in polymers.

2. Frequency Dependence

The variation of the internal friction of polymers over a wide range of frequencies has not been investigated. This is due to the experimental difficulties involved in such experiments. Fig. 7*a* shows the frequency dependence of the internal friction of polyethylene and poly(methyl methacrylate) at 30°C based on the results of several investigators [28,55,119,125,128,142,153,176].

Examination of Fig. 7 shows that in the frequency range between 10^{-3} and 10^{6} c/s poly(methyl methacrylate) has a single maximum and polyethylene two maxima in the $Q^{-1}-\nu$ curve. The origin and nature of these maxima will be discussed below. Here attention is drawn to the possible dependence of the positions of the maxima along the frequency axis and their shape on various factors. The results of the investigations presented in Fig. 7*b* make it possible to follow the effect of temperature on the shape of the $Q^{-1}-\nu$ curve. It is readily evident that an increase of temperature entails a displacement of the maximum towards higher frequencies (see also Fig. 5) and an increase in its height.

It has been shown [28] that the introduction of a plasticiser into the polymer [28] almost does not alter the position of the maximum in the $Q^{-1}-\nu$ curve for poly(methyl methacrylate) but does increase somewhat its height. However, if the molecular structure of the polymer is altered, for example by copolymerisation, the shape of the $Q^{-1}-\nu$ curve can change significantly [28]. Comparison of the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves shows that in the first case the frequency must be varied within very wide limits (at least by 5–6 powers of ten, see Fig. 1) in order to detect the required maxima, while in the second case it is sufficient to vary the temperature by less than 1–2 powers of ten (see Fig. 4).

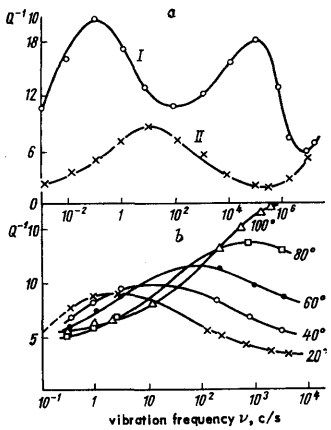


Fig. 7. *a*) Frequency dependence of the internal friction of polyethylene (curve I) and poly(methyl methacrylate) (curve II) at 30°C;
b) frequency and temperature dependence of the internal friction of poly(methyl methacrylate).

IV. THEORY OF INTERNAL FRICTION

It was noted above that in a real solid deformation does not follow exactly the stress applied to the substance from outside but lags behind it by a certain angle φ. As a result, in a periodic deformation of such a substance at a frequency ν, elastic vibration energy is dissipated. Investigations show (see Figs. 4–7) that the relative amount of energy dissipated in one cycle (or internal friction) depends on the vibration frequency and the experimental temperature. The nature of the temperature and frequency dependence of internal friction depends in turn on a multiplicity of various factors, some of which have been examined above.

The theory of internal friction should provide an answer to three questions at least: (1) why there are maxima in the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves and what is their nature; (2) why certain amorphous substances do not have maxima in the $Q^{-1}-T$ curve; (3) how various factors affect the nature of the $Q^{-1}-\nu$ and $Q^{-1}-T$ curves. The modern theory of internal friction cannot yet provide an exhaustive answer to these questions but many of aspects are now fairly clear.

The theory has developed in two main directions: one involving the phenomenological description of the principal laws governing internal friction and one involving the development of its various mechanisms on the basis of the molecular-kinetic theory. We shall examine briefly the principal results of the theory obtained in these two ways.

1. Phenomenological Theory

The phenomenological approach to the solution of the problem of the dissipation of the elastic energy of a real vibrating solid may be twofold. It is possible to solve the problem within the framework of the thermodynamics of irreversible processes after making certain simplifying assumptions about the properties of real substances. Another approach (purely formal) is based on the replacement of the real substance by a model, which reflects some definite property of the real substance. The mechanical properties of real solids, including internal friction, can be described more or less fully by a set of models. We shall begin with the latter procedure, since it has had some success [177] because of the clear-cut nature of the results obtained.

a. The model theory. We shall examine a substance which undergoes elastic deformation under stress and which can also flow. The total deformation of such a substance under the influence of a shear stress, for example, is equal to its elastic deformation and degree of flow, i.e.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \text{ or } \dot{\varepsilon} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 \qquad (8)$$

where a dot over a symbol denotes differentiation with respect to time. The rate of elastic displacement is determined from Hooke's law and the rate of viscous flow from Newton's law [see Eqn. (3)].

Hence we have from Eqn. (8)

$$\dot{\varepsilon} = \frac{\sigma}{\eta} + \frac{\dot{\sigma}}{G} . \qquad (9)$$

Let the specimen, the material of which obeys the Maxwell equation [Eqn. (9)] undergo a deformation ϵ_0 and then remain in this state. Then $\dot{\epsilon}_0 = 0$ and Eqn. (9) reduces to the following relation:

$$\frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} = 0 .$$

The solution of this differential equation has the form

$$\sigma = \sigma_0 \, e^{-\frac{G}{\eta}t} . \qquad (10)$$

Thus the decrease (relaxation) of stress in the specimen with time is exponential and is characterised by the relaxation time

$$\tau = \eta/G . \qquad (11)$$

As will be shown later, the relaxation time is a very convenient characteristic of the rate of relaxation processes in both simple and complex systems.

The behaviour of a substance which obeys the Maxwell equation can be represented by the mechanical model shown in Fig. 8. When stress is applied at a certain instant t_1, the spring is instantly extended by an amount σ/G and the piston begins to be uniformly displaced at a rate σ/η. When at another instant t_2 the stress is discontinued, the spring instantly contracts but the piston remains in the displaced state. As a result, the motion of the lower end of the model [or the deformation $\epsilon(t)$] is of the form shown in Fig. 8.

When a stress $\sigma(t) = \sigma_0 e^{i\omega t}$, which varies periodically, is applied to a Maxwell substance, dissipation of vibration energy is observed. Indeed, on substituting $\sigma(t)$ in the Maxwell equation [Eqn. (9)] and integrating the latter, we find

$$\varepsilon = I^* \sigma ,$$

$$I^* = \frac{1}{i\omega\eta} + \frac{1}{G} , \qquad (12)$$

where I^* is the reciprocal of the complex shear modulus G^* or the pliability. The following quantity is adopted as a measure of internal friction:

$$Q^{-1} = \tan\varphi = \frac{\mathrm{Im}\,(G^*)}{\mathrm{Re}\,(G^*)} = \frac{\mathrm{Im}\,(I^*)}{\mathrm{Re}\,(I^*)} . \qquad (13)$$

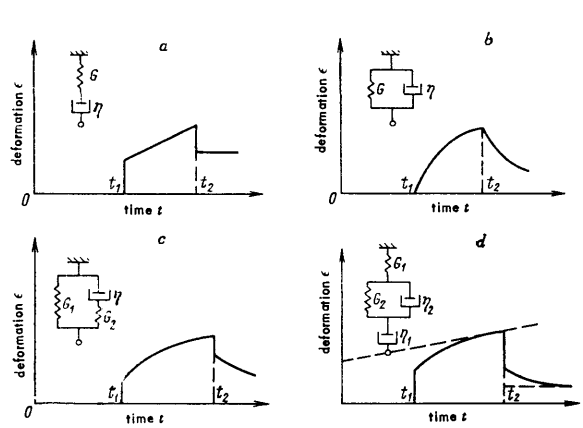


Fig. 8. Variation of the deformation with time for different types of substance (model):
a) Maxwell substance; *b*) Voigt substance; *c*) "standard linear substance"; *d*) Alfrey–Kobeko substance.

Bearing in mind Eqn. (13), we find

$$Q^{-1} = \frac{1}{\omega\tau} . \qquad (14)$$

Since the viscosity of amorphous objects is known [2,177] to decrease rapidly with temperature [in accordance with Eqn. (14)], the internal friction of a Maxwell substance should increase steadily with the temperature of the measurements. The low-frequency internal friction of certain amorphous polymers (K-18-2 resin), polypropylene, etc., does indeed increase steadily with experimental temperature, but this by no means implies that the properties of a Maxwell substance describe a real polymer satisfactorily. It was assumed above that elastic deformation takes place instantly, i.e. that the substance exhibits ideal elasticity (as well as ideal viscosity). A real substance may show a lagging elastic response, which can be represented by the mechanical model in Fig. 8*b*. This device differs from that in Fig. 8*a* in that the spring and the piston are linked in parallel and not in series. There is a significant difference between Voigt and Maxwell elements. In contrast to a Maxwell substance, the behaviour of a Voigt substance is described by the following differential equation:

$$\sigma = G \cdot \varepsilon + \eta \cdot \dot{\varepsilon} . \qquad (15)$$

It can be readily shown that the lag time (retardation) is defined by the same equation [Eqn. (11)] as the relaxation time.

In a cyclic deformation of a Voigt substance the deformation is a periodic function of time, which can be written thus:

$$\varepsilon = \varepsilon_0^* \cdot e^{i\omega t} , \qquad (16)$$

where ϵ_0^* is the complex amplitude. When Eqn. (16) is substituted in Eqn. (15), we obtain $\sigma = G^*\epsilon$, where $G^* = G + i\omega\eta$ is the complex shear modulus. We find from Eqn. (13)

$$Q^{-1} = \omega\tau . \qquad (17)$$

Comparison of Eqns. (14) and (17) shows that the variation of the internal friction of a Voigt substance with temperature [$\tau = \tau(T)$] and frequency is precisely the opposite type and therefore it does not correspond in the least to the experimental variation Q^{-1} with T and ω.

We shall now assume that the solid is a mixture of two phases, one of which is viscous [obeying Eqn. (9)] and the other is purely elastic. The mechanical model representing such an object is shown in Fig. 8*c*. If we put $G_1 = 0$ in the model, the latter becomes a Maxwell model, and if we put $G_2 = \infty$, the Voigt model is obtained.

It is not difficult to show that the differential equation corresponding to the mechanical model in Fig. 8*c* is of the form

$$\sigma + \frac{\eta}{G}\dot{\sigma} = G_1 \cdot \varepsilon + \eta\dot{\varepsilon} . \qquad (18)$$

Since this is the most general linear homogeneous equation, relating the stress, deformation, and their first derivatives with respect to time, the solids which obey Eqn. (18) are called "standard linear substances". If it is assumed that $\dot{\epsilon}$ is zero, Eqn. (18) is converted into the equation $\sigma + (\eta/G_2)\dot{\sigma} = G_1\epsilon_0$, which has a solution of the form

$$\sigma(t) = G_1 \cdot \varepsilon_0 + (\sigma_0 - G_1 \cdot \varepsilon_0)\, e^{-t/\tau_\varepsilon} ,$$

where $\tau_\epsilon = \eta/G_2$ is the relaxation time of the stress under conditions of constant deformation.

If it is assumed that $\dot{\sigma}$ is zero, then, on the basis of similar considerations, we obtain from Eqn. (18) the solution

$$\varepsilon(t) = G_1^{-1}\sigma_0 + (\varepsilon_0 - G_1^{-1}\ \sigma_0)\ e^{-t/\tau_\sigma},$$

where $\tau_\sigma = \eta/G$ is the retardation time.

Introducing the new constants τ_ϵ and $\tau_{\dot{\sigma}}$ into Eqn. (18), we obtain

$$\sigma + \tau_\varepsilon\ \dot{\sigma} = G_1(\varepsilon + \tau_\sigma\ \dot{\varepsilon}) . \qquad (19)$$

We now find the relation between the stress and deformation in standard linear substances when these quantities vary periodically with time. For this purpose, we substitute in Eqn. (19)

$$\sigma = \sigma_0\ e^{i\omega t} \text{ and } \varepsilon = \varepsilon_0^*\ e^{i\omega t}.$$

As a result we have $\sigma = G^*\epsilon$, where the complex modulus G^* is represented by the expression

$$G^* = \frac{1 + i\omega\tau_\sigma}{1 + i\omega\tau_\varepsilon}\ G_1 . \qquad (20)$$

The internal friction is now found thus:

$$Q^{-1} = \frac{\omega(\tau_\sigma - \tau_\varepsilon)}{1 + \omega^2\tau_\varepsilon\ \tau_\sigma} \qquad (21)$$

The last expression loses its significance only when $\tau_{\dot{\sigma}} - \tau_\epsilon > 0$, i.e. when the retardation time is greater than the relaxation time, As will be shown below, this does happen in real solids.

In order to represent the variation of the internal friction of a standard linear substance with angular frequency as clearly as possible, we introduce the geometrical mean§ of the times τ_ϵ and τ_σ: i.e. $\bar{\tau} = (\tau_\epsilon\tau_\sigma)^{1/2}$, and the geometrical mean of the moduli G_1 and G_2, i.e. $\bar{G} = (G_1G_2)^{1/2}$.

Then, using the equation

$$\frac{\tau_\sigma}{\tau_\varepsilon} = \frac{G_2}{G_1} , \qquad (22)$$

it is possible to transform Eqn. (21) into the following form:

$$Q^{-1} = \frac{G_2 - G_1}{\bar{G}}\ \frac{\omega\bar{\tau}}{1 + (\omega\bar{\tau})^2} . \qquad (23)$$

Eqn. (23) agrees fully with the familiar expression for Q^{-1} obtained by Zener[75] by a formal generalisation of Hooke's law, provided that we put $G_2 = M_n$ and $G_1 = M_r$, where M_n and M_r are the non-relaxation and relaxation moduli¶ respectively.

For an isotropic substance, M is understood as one of three quantities: the modulus of elasticity E, the modulus of shear G, and the modulus of bulk compressibility K. In this case the first multiplier on the right-hand side of Eqn. (23) defined the degree of relaxation of the modulus M. However, as will be shown below, for simple exponential relaxation it is more convenient to estimate the degree of relaxation of the modulus M by the quantity

$$\Delta = \frac{M_n - M_r}{M_r} , \qquad (24)$$

which is called the defect of the modulus.

§ This artificial procedure was introduced by Zener[75]. As will be seen later, $\bar{\tau}$ is in fact the really significant time, since in many cases a single average retardation time is sufficient to describe the frequency (or temperature) dependence of the decay.

¶ The final value of the stress/deformation ratio which is attained at the end of the relaxation process for the chosen mechanism with a single relaxation time.

The internal friction defined by Eqn. (23) has a maximum given by

$$Q^{-1}_{max} = \frac{1}{2}\frac{G_n - G_r}{\bar{G}} \qquad (25)$$

when

$$\omega\bar{\tau} = 1 , \qquad (26)$$

i.e. when the vibration frequency ω is equal to the reciprocal of the relaxation time $\bar{\tau}$. On either side of this maximum the internal friction decreases asymptotically to zero.

Thus a standard linear substance, i.e. a substance consisting of an elastic matrix in which viscous regions are embedded, dissipates elastic energy during periodic deformation to an appreciable extent only when Eqn. (26) holds. The relaxation time τ depends on the physical nature of the viscous region and also on its size and shape. If different amorphous regions are embedded in the elastic matrix (the basic material of the solid), then each region will have its own relaxation time τ_i and the behaviour of such a solid will be determined by the complete set of relaxation times τ_i, which leads to some "spreading" of the maximum (if the relaxation times are fairly close to one another).

Numerous experiments have shown that the relaxation time for relaxation phenomena associated with atomic and molecular rearrangement (in the field of internal forces) induced by periodic external forces varies with temperature largely according to the law

$$\tau = \tau_0 \cdot e^{H/RT} , \qquad (27)$$

where H is the heat of activation for the process, R the gas constant, and T the absolute temperature.

Since according to Eqn. (23) the internal friction Q^{-1} varies with frequency and the relaxation time in terms of the parameter $\omega\tau$, it is possible to keep the frequency ω constant and vary τ by varying the temperature. At a certain temperature T Eqn. (26) is satisfied and an internal friction maximum due to the occurrence of the relaxation phenomenon discussed above will be observed in the $Q^{-1}\omega - T$ curve.

Thus the rheological model examined makes it possible to explain the peak on the $Q^{-1} - T$ curve but it does not account for the appearance of an internal friction background, i.e. the increase of the internal friction beyond (with continuous increase of temperature) the high-temperature maximum (Fig. 4). An attempt will be made to describe the relaxation peak and the background by a model based on a series combination of Maxwell and Voigt materials, i.e. an Alfrey–Kobeko substance† (Fig. 6*d*).

The differential equation relating ϵ and σ can be obtained in this case from the following considerations. The overall deformation of an Alfrey–Kobeko substance, under the influence of shear stress for example, is equal to the sum of the deformations of the Maxwell and Voigt elements, i.e. $\epsilon = \epsilon_M + \epsilon_V$ or $\dot{\epsilon} = \dot{\epsilon}_M + \dot{\epsilon}_V$, where according to Eqn. (9) the rate of change of the deformation $\dot{\epsilon}_M$ is

$$\dot{\varepsilon}_M = \frac{\dot{\sigma}}{G_1} + \frac{\sigma}{\eta_1}$$

and according to Eqn. (15) that of $\dot{\epsilon}$ is

$$\dot{\varepsilon}_V = \frac{\sigma}{\eta_2} - \frac{G_2}{\eta_2}\ \varepsilon_V . \qquad (28)$$

† This model is sometimes called the four-element model.

On adding together ϵ_M and $\dot{\epsilon}_V$, differentiating the resulting equation once more with respect to time, and eliminating ϵ_V and $\dot{\epsilon}_V$ from these two equations, we obtain with the aid of Eqn. (33) the required differential equation in the following form:

$$\ddot{\sigma}+\left(\frac{1}{\tau_1}+\frac{G_2+G_1}{G_2}\cdot\frac{1}{\tau_2}\right)\dot{\sigma}+\frac{\sigma}{\tau_1\tau_2}=G_1\ddot{\varepsilon}+\frac{G_1\dot{\varepsilon}}{\tau_2} \quad , \qquad (29)$$

where the relaxation times are

$$\tau_1=\eta_1/G_1; \quad \tau_2=\eta_2/G_2 \quad . \qquad (30)$$

On substituting in Eqn. (29)

$$\sigma=\sigma_0\, e^{i\omega t} \text{ and } \varepsilon=\varepsilon_0^*\, e^{i\omega t} \quad ,$$

we obtain

$$\sigma=G^*\,\varepsilon,$$

where

$$G^*=\frac{-G_1\omega^2+i\omega G_1/G_2}{-\omega^2+i\omega\left(\frac{1}{\tau_1}+\frac{G_2+G_1}{G_2}\,\frac{1}{\tau_2}\right)+\frac{1}{\tau_1\tau_2}} \quad . \qquad (31)$$

According to Eqn. (13),

$$Q^{-1}=\frac{1+\omega^2\tau_2^2+\frac{G_1}{G_2}\omega^2\tau_1\tau_2}{\omega\tau_1\left(\frac{G_2+G_1}{G_2}+\omega^2\tau_2^2\right)} \quad . \qquad (32)$$

Internal friction at a constant frequency depends significantly on the relation between η_1 and G_1 on the one hand and η_2 and G_2 on the other. If, for example, $G_2 \gg G_1$, then the deformation of an Alfrey–Kobeko substance will be determined mainly by the deformation of the Maxwell element and therefore the internal friction must be calculated in this case from a formula analogous to Eqn. (14). Indeed, if $G_2=\infty$, it follows from Eqn. (32) that $Q^{-1}=1/\omega\tau_1$, i.e. Eqn. (14) obtains. If, on the other hand, $G_1 \gg G_2$ and $\eta_1 \gg \eta_2$, the deformation of an Alfrey–Kobeko substance is determined almost entirely by the deformation of the Voigt element. In the limit, when $G_1=\infty$ and $\eta_1=\infty$, we obtain from Eqn. (32) $Q^{-1}=\omega\tau_2$, i.e. Eqn (17), which applies to a Voigt substance.

For other relations between G_1 and G_2 and between η_1 and η_2, a maximum and a background can appear on the Q^{-1}_{ω}–T curve. Fig. 8*a* confirms this. The average relaxation time τ_2 was found from the data of Nolle et al. [178] (Fig. 5). The ratio $G_1/G_2=0.16$ was obtained from Eqn. (32) on the assumption that the maxima on the theoretical and experimental Q^{-1}–T curves are of the same magnitude. We now find that an Alfrey–Kobeko substance does indeed reflect the properties of real solids more fully than a standard linear substance. With its aid, it is possible to explain qualitatively‡ the temperature variation for certain polymers. However, many polymers have not one but several broad and narrow maxima on the Q^{-1}–T curve (Fig. 4).

‡ No model with a single relaxation time can describe satisfactorily a real Q^{-1}–T curve whatever the relations between the moduli G_i and the viscosities η_i, since only absolutely rigid molecules can have a single relaxation time. The molecules of a real polymer are flexible. As a result of their flexibility, the relaxation processes in polymers can be described only with the aid of an extensive set or a continuous spectrum of relaxation times. However, when the maxima on the Q^{-1}–T curve are fairly narrow, they can be described satisfactorily also with a single average (or most probable) relaxation time. See also Refs. 6 and 179.

The introduction of a large number of elastic and viscous elements makes it possible to set up complex rheological models, which are consistent with many relaxation times and which provide the best approximation to various properties of a real polymer [2,5,177,180–183]. A one-dimensional complex rheological model characterised by n relaxation times with a zero equilibrium stress leads to $n-1$ maxima and an internal friction background curve. However, while it is still possible to attribute some definite physical significance to the elements of an Alfrey–Kobeko substance [177], this cannot be done for the elements of a complex rheological model§. Furthermore, a linear rheological model cannot be used to find the temperature variation of the square of the frequency, from which the temperature variation of the modulus of shear is estimated and therefore it cannot yield the correct temperature variation of internal friction, since the latter depends on the frequency.

A less formal approach, which is to some extent free of the above defects, whereby it is possible to solve from the very beginning the three-dimensional problem of the dissipation of the energy of elastic vibrations, is provided by the thermodynamics of irreversible processes.

b. Thermodynamic theory. The principle of the thermodynamic theory of relaxation phenomena in solids (isothermal case) was put forward by Finkel'shtein and Fastov [184]. Later this theory was extended to the case of non-isothermal deformations [185–189]. The following expression has been obtained for the stress tensor for a homogeneous isotropic body [188]:

$$\sigma_{ik}=K\cdot e_{ll}\cdot\sigma_{ik}+2G\left(e_{ik}-\frac{1}{3}e_{ll}\cdot\delta_{ik}\right)+\eta_2/\tau_2\int_{-\infty}^{t}\dot{e}_{ll}(t')\,e^{\frac{t'-t}{\tau_3}}dt'+\frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\left[\dot{e}_{ik}(t')-\frac{1}{3}\dot{e}_{ll}(t')\,\delta_{ik}\right]e^{\frac{t'-t}{\tau_1}}dt'-C\cdot\delta_{ik}\cdot C_v\int_{-\infty}^{t}\dot{T}(t')\,e^{\frac{t'-t}{\tau_3}}dt'-K\cdot\alpha\cdot\delta_{ik}\int_{-\infty}^{t}\dot{T}(t')\,e^{\frac{t'-t}{\tau_3}}dt' \quad . \qquad (33)$$

Here K is the isothermal modulus of all-sided compression, G the modulus of shear, η_2 the bulk viscosity, η_1 the coefficient of the shear relaxation of the viscosity, τ_2 and τ_1 are the relaxation times of the bulk and shear viscosities C is a constant, C_v the heat capacity per unit volume of the substance at constant volume, α the thermal conductivity, and τ_3 the thermal relaxation time defined by the expression

$$\tau_3\simeq\frac{C_l^2}{\varkappa'\omega^2} \quad , \qquad (34)$$

where $\varkappa'$ is the thermal diffusivity, C_l the velocity of longitudinal sound waves, and ω the angular frequency. The variation of τ_3 with frequency can be accounted for by the fact that an increase of the frequency entails an increase in the size of the regions between which the relaxation of the thermal flux takes place. For polymers (as for metals), temperature relaxation need be taken into account only in the hypersonic region [as is readily evident from Eqn. (34)]. In the region of sonic and ultrasonic frequencies $\omega\tau_3 \gg 1$.

For adiabatic deformation in this frequency range we have [188]

$$\sigma_{ik}=K^{ad}\cdot e_{ll}\sigma_{ik}+2G\left(e_{ik}-\frac{1}{3}e_{ll}\cdot\delta_{ik}\right)+\eta_2^{ad}/\tau_3\cdot\delta_{ik}\int_{-\infty}^{t}\dot{e}_{ll}(t')\,e^{\frac{t'-t}{\tau_3}}dt'+\frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\left[e_{ik}(t')-\frac{1}{3}e_{ll}(t')\,\delta_{ik}\right]e^{\frac{t'-t}{\tau_1}}dt', \qquad (35)$$

§ For a physical justification of rheological models, see Zelenev and Molotkov [181,182].

where

$$K^{ad} \equiv K + T_0\alpha^2\frac{K^2}{C_v} \qquad (36)$$

$$\eta_2^{ad} = \eta_2 + CT_0\alpha K\cdot\tau_2 \quad . \qquad (36')$$

We now use Eqn. (35) for the stress tensor to calculate the internal friction and the absorption coefficient of longitudinal and transverse elastic waves.

For a pure shear, for example low-amplitude torsional vibrations, $\epsilon_{ll} = 0$, and therefore

$$\sigma_{ik} = 2G\cdot\varepsilon_{ik} + \frac{2\eta_1}{\tau_1}\int_{-\infty}^{t}\varepsilon_{ik}(t')e^{\frac{t'-t}{\tau_1}}dt' \quad .$$

If the deformation is a periodic function of time, then

$$\varepsilon_{ik} = \varepsilon_{ik}^{(0)}\cdot e^{i\omega t} \quad ,$$

and the generalised Hooke's law is written in the following form:

$$\sigma_{ik} = G^*\cdot\varepsilon_{ik} \quad ,$$

where the complex modulus of shear is

$$G^* = G + \frac{i\omega\eta_1}{1+i\omega\tau_1}$$

or

$$G^* = G + \frac{(\omega\tau_1)^2}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} + \frac{i\omega\tau_1}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} \quad . \qquad (37)$$

The real component of the complex modulus is usually employed as the dynamic modulus, i.e.

$$G_\omega = G + \frac{(\omega\tau_1)^2}{1+\omega^2\tau_1^2}\cdot\frac{\eta_1}{\tau_1} \quad . \qquad (38)$$

We find from the last expression (if the temperature relaxation at hypersonic frequencies is disregarded, as was done above)

$$G_\infty = G + \eta_1/\tau_1 \quad G_0 = G \quad . \qquad (39)$$

Taking into account Eqns. (38) and (39), we obtain the modulus of shear which determines the degree of relaxation:

$$\Delta'_\omega = \frac{G_\infty - G_\omega}{G_0} = \frac{\Delta'_0}{1+\omega^2\tau_1^2} \quad , \qquad (40)$$

where

$$\Delta'_\omega = \frac{G_\infty - G_\omega}{G_0}$$

is the maximum defect of the shear modulus. Bearing in mind Eqn. (13), we find from Eqn. (37)

$$Q^{-1} = \frac{\Delta'_0\,\omega\tau_1}{1+\frac{G_\infty}{G_0}\omega^2\tau_1^2} \quad . \qquad (41)$$

Eqn. (41) is identical, to within the multiplier G_∞/G_0 in its denominator, with Eqn. (23) obtained above from model hypotheses for a standard linear body, if G_2 is identified with G_∞ and G_1 with the modulus G_0. Therefore all that has been said above about Eqn. (23) applies also to Eqn. (41). Furthermore, one may say that the moduli G_2 and G_1 now acquire a completely definite physical significance, defined by Eqn. (39).

Repeating the above reasoning and operations, we find for bulk compression

$$Q^{-1} = \frac{\Delta''_0\,\omega\,\tau_2}{1+\frac{K^{ad}}{K_0^{ad}}\omega^2\tau_2^2} \quad , \qquad (42)$$

where

$$\Delta'' = \frac{K_\infty^{ad} - K_0^{ad}}{K_0^{ad}} \quad . \qquad (43)$$

Evidently the nature of the variation of Q^{-1} with the parameter $\omega\tau$ does not change.

We now find the absorption coefficient α. Suppose that a transverse wave with frequency ω has the wave vector $\vec{k}$ ($k_x = k$, $k_y = 0$, $k_z = 0$), i.e. it is planar and is propagated along the x axis. It will be assumed that the wave is propagated in an infinite relaxing medium, described by the stress tensor (35). On substituting the non-zero components σ_{xy} and σ_{xz} is the equation of motion

$$\rho\frac{\partial^2\varepsilon_i}{\partial t^2} = \frac{\partial\sigma_{ik}}{\partial x_k} \quad , \qquad (44)$$

we find

$$\left.\begin{aligned} -\rho\omega^2A_y &= -k^2GA_y + i\frac{k^2A_y\,\omega\eta_1}{1-i\omega\tau_1} \\ -\rho\omega^2A_z &= -k^2GA_z + i\frac{k^2A_z\omega\eta_1}{1-i\omega\tau_1} \end{aligned}\right\} \quad . \qquad (45)$$

The square of the wave vector, obtained with the aid of Eqns. (45), is

$$k^2 = \frac{\rho\omega^2}{G}\frac{1+2\omega^2\tau_1^2+i\omega\tau_1}{1+4\omega^2\tau_1^2} \quad . \qquad (46)$$

In the limiting case of low frequencies ($\omega\tau_1 \ll 1$), i.e. when the period of the sound wave is large compared with the relaxation time, Eqn. (46) yields the following result:

$$k = \omega\sqrt{\rho/G} + i\frac{\omega^2\tau_1}{2}\sqrt{\rho/G} \quad , \qquad (47)$$

i.e. decay takes place, due to the presence of shear viscosity with the coefficient

$$\alpha'_t = \frac{\omega^2\tau_1}{2}\sqrt{\rho/G} \quad , \qquad (48)$$

which is proportional to the square of the frequency, in agreement with the familiar expression for the absorption coefficient[1]: $\alpha_t = \omega^2\eta_1/2\rho C_t^3$, provided that one puts $\eta_1 = G\tau_1$.

As was to be expected, the rate of propagation of the wave

$$C'_t = \frac{\omega}{\mathrm{Re}\,(k)} = \sqrt{G/\rho} \qquad (49)$$

is independent of frequency. In the opposite limiting case of high frequencies ($\omega\tau_1 \gg 1$), we find from Eqn. (46) for the absorption coefficient

$$\alpha''_t = \frac{1}{4\tau_1}\sqrt{\rho/2G} = \frac{1}{4\tau_1 C''_t} \quad , \qquad (50)$$

where the velocity of sound C''_t is

$$C''_t = \sqrt{\frac{2G}{\rho}} \quad . \qquad (51)$$

Both the absorption coefficient and the velocity of sound are to a first approximation independent of frequency at

high frequencies. In a more accurate expression the frequency dependence of both quantities is taken into account by the multiplier $1 - 1/8\omega^2\tau_1^2$, and the first expression in Eqn. (50) should be used for α_t''.

We shall now consider the propagation of a longitudinal sonic wave in an infinite relaxing medium. The only non-zero terms, the component of the displacement vector ϵ_x and the component of the deformation tensor $\epsilon_{xx} = ik\epsilon_x$, yield the following expression for the corresponding component of the stress tensor (33):

$$\sigma_{xx} = ik\varepsilon_x \cdot K + {}^4/_3 iG \cdot K \cdot \varepsilon_x + \frac{k\omega\eta_2^{ad}}{1-i\omega\tau_2}\varepsilon_x + {}^4/_3\frac{k\omega\eta_1}{1-i\omega\tau_1}\varepsilon_x + \frac{k\omega\chi}{1-i\omega\tau_3}\varepsilon_x, \quad (52)$$

where the conversion from the temperature function to the deformation function is performed with the aid of Eqn. (1), with χ defined thus:

$$\chi \equiv \tau_3\ \alpha^2 K T_0/C_v\,. \quad (53)$$

On substituting Eqn. (52) in the equation of motion (44), we find the square of the wave number:

$$k^2 = \rho\omega^2\left[K + {}^4/_3 G - i\left(\frac{\omega\eta_2^{ad}}{1-i\omega\tau_2} + {}^4/_3\frac{\omega\eta_1}{1-i\omega\tau_1} + \frac{\omega\chi}{1-i\omega\tau_3}\right)\right]. \quad (54)$$

At low frequencies $\omega\tau_1$ and $\omega\tau_2$ are both much less than 1 and, as pointed out earlier, $\omega\tau_3 \gg 1$. Bearing this in mind, we obtain the following expression for the wave number:

$$k \simeq \sqrt{\frac{\rho\omega^2}{K^{ad}+{}^4/_3 G}}\left(1 + \frac{i\omega}{2}\frac{{}^4/_3\eta_1 + \eta_2^{ad} + \chi/\omega^2\tau_3^2}{{}^4/_3 G + K^{ad}}\right). \quad (55)$$

The rate of propagation of longitudinal waves is found from the real part of this expression:

$$C_l' = \sqrt{\frac{K^{ad}+{}^4/_3 G}{\rho}}\,. \quad (56)$$

The imaginary part of Eqn. (55) yields the absorption coefficient for longitudinal waves:

$$\alpha_l' = \frac{\omega^2}{2}\frac{\sqrt{\rho}}{(K^{ad}+{}^4/_3 G)^{3/2}}\left({}^4/_3\eta_1 + \eta_2^{ad} + \frac{\chi}{\omega^2\tau_3^2}\right). \quad (57)$$

In the region of high but not hypersonic frequencies the condition $\omega\tau_1 \gg 1$ holds for all relaxation times. In this case we obtain from Eqn. (54)

$$k \simeq \frac{\omega\sqrt{\rho} + \frac{i\sqrt{\rho}}{2}(\eta_2^{ad}/\tau_2^2 + {}^4/_3\eta_1/\tau_1 + \chi/\tau_3^2)}{[K^{ad} + \eta_2^{ad}/\tau_2 + {}^4/_3(G + \eta_1/\tau_1)]^{1/2}}\,, \quad (58)$$

whence

$$C_l'' = \frac{1}{\sqrt{\rho}}[K^{ad} + \eta_2^{ad}/\tau_2 + {}^4/_3(G + \eta_1/\tau_1)]^{1/2} \quad (59)$$

and

$$\alpha_l'' = \frac{1}{2(C_l'')^3}\left(\eta_2^{ad}/\tau_2^2 + {}^4/_3\eta_1/\tau_2 + \frac{\alpha^2 K^2 T_0 \varkappa'}{C_v (C_l'')^2}\omega^2\right). \quad (60)$$

Thus the viscosity component of the absorption coefficient yields a constant term to a first approximation and the component due to the principal thermal conductivity yields a quadratic relation in frequency which does not differ from the corresponding additional term in the expression for α_l', as in both cases the condition $\omega\tau_3 \gg 1$ holds.

Summarising, one may say that at frequencies between 10^{-3} and 10^8 c/s, which we examined above (Figs. 4 and 5), the important factor is viscous relaxation (shear or bulk), which in the case of homogeneous isotropic solids is characterised by a single relaxation time. Consequently, according to Eqns. (41) and (42), a homogeneous isotropic body is characterised by a peak on the Q^{-1}–$\omega\tau$ curve and the absence of background. The Q^{-1} background can appear only if the body is inhomogeneous, i.e. has two (or more) relaxation times. An example of such a body is a mixture of amorphous polymers, partially crystalline polymers, cross-liked polymers, polymers containing impurities, etc.

A thermodynamic examination of the problem for the case of an inhomogeneous body with two relaxation times has been made by Shermergor and Meshkov[190]. The results of the theory have been examined using polycrystalline aluminium as an example. The form of the Q^{-1}–T curve is similar to that of the analogous curve which the present author obtained for poly(methyl methacrylate) on the basis of model hypotheses (Fig. 9*a*).

Under conditions of cyclic deformation, relaxation processes occur at different rates and at different sites of an inhomogeneous polymer and therefore its behaviour is described by a whole spectrum (discrete or continuous) of relaxation times. However, the spectrum of relaxation times in a solid polymer can be due not only to different rates of the relaxation process in different regions of the inhomogenous body but can also be caused by the presence of various relaxation mechanisms resulting from the flexibility of the molecules[2,7–11,75]. If several independent relaxation processes, each characterised by its own relaxation time τ_i, take place simultaneously in the polymer, the internal friction of the latter, for example in the presence of shear vibrations, is defined by the expression[8,9,75]

$$Q^{-1} = \sum_{i=1}^{n}\frac{\Delta_i^{(0)}\cdot\omega\tau_i}{1 + \left(\frac{G_\infty}{G_0}\right)_i(\omega\tau_i)^2}\,. \quad (61)$$

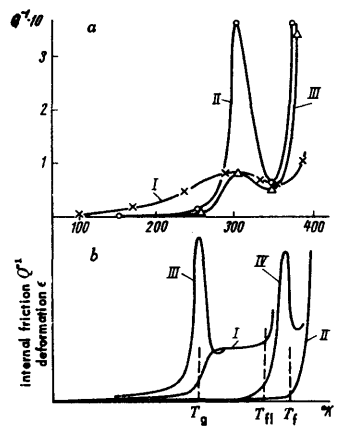


Fig. 9. *a*) Temperature dependence of the internal friction of poly(methyl methacrylate): I) experimental curve[18] for $\nu = 0.4$ c/s; II) and III) theoretical curves [II) $G_1/G_2 = 1$; III) $G_1/G_2 = 0.16$; $\tau_1 = 100\tau_2$; $\nu = 0.4$ c/s];
b) schematic representation of the temperature dependence of the deformation (curves I and II) and internal friction (curves III and IV) of polymers: I) and III) amorphous polymers; II) and IV) crystalline polymers.

Finally, for a continuous distribution of the relaxation constants, which frequently obtains in inhomogeneous materials, the internal friction is defined by the expression[9,75]

$$Q^{-1}=\int_{-\infty}^{+\infty}\frac{\psi(\tau)\,\omega\tau}{1+\left(\frac{G_\infty}{G_0}\right)_{cp}\omega^2\tau^2}\,d(\ln\tau)\ , \qquad (62)$$

where $\Psi(\tau)$ is an unknown distribution function difficult to determine experimentally. It can be found from the condition

$$(\Delta_0)_{cp}=\int_{-\infty}^{+\infty}\psi(\tau)\,d(\ln\tau)\ , \qquad (63)$$

where $(\Delta_0)_{av}$ is the average defect of the modulus found experimentally; this requires the inversion of the integral, which introduces a considerable inaccuracy into the final result.

It is evident from all that has been said above that the phenomenological theory describes fairly completely the frequency and temperature dependence of internal friction in homogeneous and inhomogeneous isotropic solids. The theory of internal friction in anisotropic materials has only just begun to be developed. For example, an expression has been obtained[191] for the stress tensor in a homogeneous anisotropic crystal and it has been shown that the stress tensor components σ_{ik} undergo relaxation to their equilibrium values $\bar{\sigma}_{ik}$, but the relaxation does not involve a simple exponential decay to the equilibrium value, as happens for an isotropic medium, but is determined by the entire set of relaxation times τ_{ik}. In the general case (crystals of the triclinic system) the relaxation of stresses in an isotropic medium is determined by six relaxation times τ_{ik} corresponding to six independent components of the stress tensor.

2. Molecular-Kinetic Description

In contrast to the phenomenological theory, in which the processes responsible for the dissipation of energy by the vibrating body are not considered in detail, the molecular-kinetic theory of internal friction should account for the principal features of the temperature and frequency dependence of the internal friction of solids (and the effect of various factors on the variation of Q^{-1} with T and ν) by a detailed analysis of the molecular processes which constitute its basis. However, the extremely complex structure of polymer molecules, the wide variety of possible types of polymers with the same chemical composition and molecular weight, and other distinctive features, compared with low-molecular compounds and metals, led to considerable difficulties in the development of a molecular-kinetic theory of internal friction.

The starting point of the molecular-kinetic description of the relaxation phenomena consists of hypotheses about the structure of the molecule and about the existence of polymers in various physical states—three amorphous and one crystalline. A clear idea about these physical states is obtained by plotting the deformation of the polymer (developing in a definite period at a given temperature and with specified stress) against temperature. For an amorphous substance, this plot[2], which has been called the thermomechanical curve, should have the form shown schematically by curve I in Fig. 9*b*. The two vertical dashed lines corresponding to temperatures T_g and T_{fl} divide curve I into three regions. The first (from 0°K to T_g) corresponds to the solid vitreous state of the substance, the second to the rubberlike state, and the third to the viscous state.

Since on cooling the polymers solidify (are converted into a glass) in the temperature range arbitrarily denoted by the temperature T_g, the latter has been called the glass point. At temperatures much lower than T_g the polymer molecules cannot change their shape and relative positions. The conformation of the molecular chain is "frozen". However, below T_g individual groups of atoms, which usually form part of the side-chain but can be linked also to the main chain, retain their mobility[192-195].

Near the temperature T_g and above it (but below T_{fl}) a change in the shape of the molecules is observed but not their mutual displacement, the latter being possible near the flow temperature T_{fl} and above it. The temperature range between T_g and T_{fl}, in which the polymer is a rubberlike material, is greater with higher molecular weights. We may note that the same amorphous polymer at the same temperature is capable of exhibiting the properties of vitreous, rubberlike, and viscous-fluid materials, depending on the rate of deformation. Therefore the temperatures T_g and T_{fl} are not physical constants but depend on the rate of deformation or the frequency of the changes in deformation. For example, at a low rate of deformation ($\nu \simeq 1$ c/s) $T_g \simeq 315$°K for poly(methyl methacrylate)[177]. The maximum in the internal friction of poly(methyl methacrylate) occurs at approximately the same temperature (Fig. 9*a*). This relation (schematically shown by curve III in Fig. 9*b*) is observed also for other amorphous polymers. This finding led to the hypothesis[104,107,117,119] that the high-temperature maximum (α-peak) in the internal friction of amorphous polymers is due to a change in the segmental mobility¶ of the molecule.

Similarly the first internal friction peak (or the sharp rise of the Q^{-1}–T curve near the melting point) of crystalline polymers (Fig. 4 and the schematic curve IV in Fig. 9*b*) is attributed[104,117,145] to the increase in the segmental mobility of the polymer molecule on fusion of the individual crystallites.

The nature of the remaining Q^{-1}–T peaks located below the first along the temperature axis may be extremely varied. For example, the second peak (the β-peak) on the Q^{-1}–T curve for poly(methyl methacrylate) is thought to be caused[152,158] by the rotation of the O=C–OCH_3 side-groups between positions of relative stability via an energy barrier, which reflects the steric hindrance due to the methyl groups attached to the same chain atoms. The study of copolymers of variable composition[158] shows that the elimination of the steric hindrance on replacing methacrylate by acrylate results in the disappearance of the loss mechanism; the replacement of the methyl ester group by any rigid and bulky ester group leads to the same effect, which can be explained by the hindrance to the rotation of these groups. On the other hand, the substitution of a more flexible ester group displaced the effect of this mechanism towards higher frequencies and raises the slope of the curves. Although the steric hindrance associated with the existence of two substituted chain atoms is probably responsible for the second peak on the curve for polymethacrylates, secondary loss mechanisms are also observed for polymers whose chains contain monosubstituted atoms

¶ In some cases it can consist of the sum of the contributions Q_α^{-1} and Q_β^{-1} due to the motion of side-groups[196].

but these are usually shown at higher frequencies or at lower temperatures and have smaller maxima. For example, the second peak on the Teflon and poly(vinyl chloride) curves is attributed to an amorphous phase [31]—to conformational changes in the amorphous phase relative to short polar chains [111]. The nature of such local motion is obscure.

The second peak (β-peak) on the polyethylene curve is associated either with the presence of an amorphous phase or with branching of the polyethylene molecules [107,117,126]. The third polyethylene peak (γ-peak) is attributed to the rearrangement of adjacent CH_2 groups [5].

The motion of methyl groups gives rise to the peak on the $Q^{-1}-T$ curve for polypropylene (at about 13°K). [197] Other cases are also known where the side-groups can be involved in motion at low temperatures, while the main skeleton of the molecules shows little mobility, which gives rise to peaks on the $Q^{-1}-T$ curve [104,192,198].

The cases examined above suggest that the observed maxima on the $Q^{-1}-T$ curves for solid polymers can be divided into two groups: the group of the so called principal maximum (α-peak in polyethylene and other substances) and the group of secondary maxima (β-, γ-, etc., peaks)†. The principal maximum is due to change in the mobility of the side-groups or individual small atomic groups of the main chain or the side-chains, which take part in thermal motion as independent elements. The position of the principal maximum is significantly influenced by the size of the side-groups. It has been shown [104] that, as the volume of the side-groups increases, the mobility of the main molecular chain falls and therefore at a constant frequency the principal maximum is displaced towards higher temperatures. At a constant temperature the maximum occurs at lower frequencies.

All these findings demonstrate that the temperature and frequency dependence of internal friction is indeed determined by the type of molecular motion. The type of molecular motion in turn depends on the composition and structure of the polymer and also on external factors (temperature, pressure, radiation, the medium surrounding the polymer, etc). Therefore, in their studies of the effect of composition, structure, and the factors indicated above on the nature of the temperature and frequency dependence of internal friction, various investigators [31,104,107,111,117,119,197,198] were able to arrive at the conclusions discussed above. However, even for a relatively simple molecular system such as polyethylene, it is impossible to make a unique interpretation of the results obtained. This also applies to other polymers which have been investigated [31,104,111]. This ambiguity can be eliminated to some extent by comparing the results of studies of mechanical and dielectric losses with those obtained by the nuclear magnetic resonance method.

V. COMPARISON OF THE RESULTS OF STUDIES ON MOLECULAR MOTION IN POLYMERS, OBTAINED BY DIFFERENT METHODS

1. Mechanical and Dielectric Losses

The first study in which mechanical properties were investigated in order to compare them with dielectric properties is that of Mikhailov and Kirilina [200] more than 25 years ago. They established that at a frequency of about 500 c/s the temperature maxima in Q^{-1} and tan φ_e for ebonite approximately coincide. A similar result was obtained by other investigators [175,201], for ebonite, rubber, and polyisobutylene. Comparison of these results, obtained at low deformation amplitudes, reveals a direct relation between mechanical and electric relaxation (see also Refs. 164, 202, 203).

Fig. 10 presents the results of a study of the temperature variation of the mechanical and dielectric losses for polyethylene [131] and poly(vinyl chloride) [204]. Evidently the $Q^{-1}-T$ and tan φ_e-T curves are of similar form. The form is similar but not identical, since even at the same frequencies (Fig. 10*b*) there is a perceptible difference in the positions of the maxima in Q^{-1} and tan φ_e along the temperature axis [164]. At a frequency of 2×10^6 c/s the tan φ_e maximum (not shown in Fig. 10*b*) is 27 deg below [204] the maximum in Q^{-1}. At a frequency of 3×10^5 c/s the temperature difference is 11 deg and at a frequency of 10^3 c/s only 8 deg. The difference for ebonite at 500 c/s is 3 deg. Such a slight difference suggests that at low deformation amplitudes (when we deal mainly with orientation relaxation), dielectric and mechanical relaxations have a common mechanism. The mechanical and dielectric losses are probably associated with the same form of thermal motion in the polymer [6]. This is shown by the agreement between the activation energies and between the relaxation times [175,200,201,204,205].

It is readily seen (Fig. 10*b*) that at high frequencies (above 10^4 c/s) the maximum in dielectric losses is higher than the maximum in mechanical losses, while at low frequencies (below 10^4 c/s) the opposite relation holds. The opposite variation of the heights of the maxima in Q^{-1} and tan φ_e with frequency is due to the fact that the maximum in dielectric losses is determined by the polarity of the vibrating side-groups or radicals while the maximum in mechanical losses is due to their mass.

The polarity of the side-groups determines not only the frequency but also the position of the maximum along the

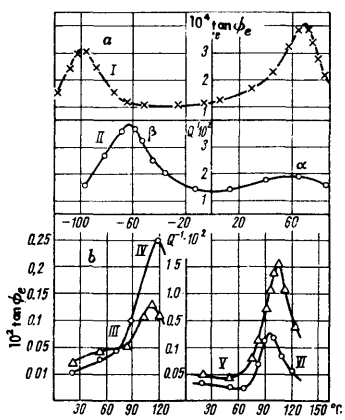


Fig. 10. Temperature dependence of the dielectric loss factor (curves I, IV, and VI) and internal friction (curves II, III, and V) of low-pressure polyethylene (*a*) and poly(vinyl chloride) (*b*):
I) $\nu \sim 5 \times 10^3$ c/s; II) $\nu = 2 \times 10^6$ c/s; III) and IV) $\nu = 3 \times 10^5$ c/s; V) and VI) $\nu = 10^3$ c/s.

† The same subdivision obtains also for rubberlike polymers [59,199].

temperature axis. With increasing dipole moments of the groups, the maximum in tan φ_e is displaced towards higher temperatures, which corresponds to a decrease of mobility with polarity [205]. An increase of the length of the racicals bound chemically to the main chain, while leaving the dipole moment virtually unaltered, causes a diplacement of the tan φ_e maximum towards lower temperatures [206].

Molecular relaxation observed by the dielectric loss method can be divided (like the mechanical relaxation examined above) into two main types: the relaxation of polar groups and the relaxation of the same polar groups together with sections of the main chain, i.e. the relaxation of segments [6,193,207,208]. This has been established for polymers with a wide variety of structures (linear and branched, polymers containing rings in the chain, partially crystallised polymers, and fully amorphous polymers [6,193,208,208]). The losses due to the first type of relaxation are called dipole-radical losses and those due to the second type are called dipole-elastic losses. Usually losses of the first type are observed in a definite temperature range corresponding to the vitreous state of the polymer, while losses of the second type occur above the glass point T_g‡. However, the dipole-radical losses are not a feature of the relaxation of the vitreous state of polymers but can be observed in the rubberlike state, if the period of application of the electric field is comparable with the relaxation time for losses of this type at the chosen temperature [193].

Thus dipole-radical losses reflect the molecular relaxation process which is due to the motion of polar side-groups, while the main chain remains stationary during a period comparable to the vibration period of the applied electric field. If the period of the applied field is sufficiently high, then at certain temperatures it is possible to observe the dipole-elastic losses caused by the displacement of segments together with the polar side-groups. In linear polymers a segment may consist of 2–4 methylene groups [209,210].

The characteristics of losses of the first and second types are also determined by the factors described above. For example, the positions of the temperature and frequency maxima in tan φ_e for dipole-radical losses are independent of the presence of low-molecular impurities [211], but the positions for dipole-elastic losses do depend considerably on such impurities. The relaxation times of the corresponding process decrease under these conditions. The cross-linking of the macromolecules, which impedes their motion and increases the relaxation time of the dipole-elastic losses, has the opposite effect [212,213]. According to the few data available in the literature, the extension of polymer specimens, leading to the orientation of the main chain, increases the relaxation time of dipole-elastic losses but does not affect the relaxation time of dipole-radical losses [214]. Losses of both kinds are considerably influenced by a change in the chemical structure of the monomer unit of the polymer chain. Both polar and non-polar groups, which can be attached either directly to the main chain or to a side-radical, have an effect. For example in a comparative study of mechanical and dielectric losses it has been shown [152] (see Table, entries 13 and 17) that the replacement of the methyl group in the α-position in poly(methyl methacrylate) by a polar group such as CCl, which occupies approximately the same volume, greatly inhibits the segmental motion of the macromolecules. The effects of polarity are enhanced when CH_3 groups are replaced by CN. Comparative study of the temperature variation of Q^{-1} and tan φ_e for low-pressure polyethylene (Fig. 9*a*) [56,131,193] permits the preliminary conclusion that the low temperature β-maximum is due to the "unfreezing" of segmental motion and the high-temperature α-maximum is due to the incipient fusion of poorly formed crystals. The nature of the maxima in Fig. 10*b*, which have been described in detail [204], is not sufficiently clear. The maximum in tan φ_e is due to dipole-elastic losses, i.e. the motion of segments. However, the number of molecular units in the segment remains unknown. The situation is the same as regards the explanation of the γ-maximum on the Q^{-1}–T curve for high-pressure polyethylene, the macromolecules of which are much more branched than for low-pressure polyethylene. The dielectric method does not yield the required information concerning the nature of this maximum. Some workers have simply attributed this maximum to the thermal motion of the parts of macromolecules constituting the amorphous regions of the polymer [215-217].

As mentioned above, the NMR method is very suitable for the investigation of molecular motion. Using this method, one of the first direct demonstrations of rotation of groups about bonds in polymer chains has been achieved [248]. Bearing this in mind, an attempt will be made to resolve, with the aid of the NMR method, the obscure problems concerning the nature of the Q^{-1} maxima, for example on the curves for high-pressure polyethylene and poly(vinyl chloride).

2. Mechanical Losses and Nuclear Magnetic Resonance

The application of nuclear magnetic resonance in the study of molecular motion is based on the observation of changes in the width of the absorption line, which becomes narrower with increasing rate of molecular motion [219-222]. Using nuclear magnetic resonance [223], it is possible to determine both the nature of the mobile group in the polymer and the mode and rate of its motion.

The first comparison of NMR data with results obtained by the internal friction method was made for rubber [224] soon after the discovery of NMR. Some investigators [225-229] have examined the relation between NMR data and the internal friction of polyisobutylene, poly(methyl methacrylate), poly(vinyl chloride), polyethylene, and other polymers. Much work has been done on the relation between mechanical, dielectric, and nuclear resonance absorption in many polymers (see, for example, Refs. 224, 225).

Fig. 11 presents the results of studies on the temperature variation of the internal friction [104,117,119,230] and the nuclear resonance absorption line width [231,232] of high-pressure polyethylene and poly(vinyl chloride) [104,231]. It is seen (Fig. 11*b*) that the absorption line width ΔH varies with temperature similarly to the shear modulus G. In the range 350–360°K, corresponding to the glass point of poly(vinyl chloride), a sharp change in G and ΔH and a distinct maximum in Q^{-1} are observed. The sharp change in ΔH takes place near the transition temperatures which are observed refractometrically [233,234] and by heat capacity measurements [235]. The correlation between the transitions observed by the NMR method and the conversion to the vitreous state observed by other methods makes it possible to relate these transitions to the onset of motion of main-chain segments [194]. However, the number of monomer units in a segment has not been determined with adequate precision. We may note

‡ Sometimes "degeneracy" of the dipole-elastic processes is observed at high temperatures [6].

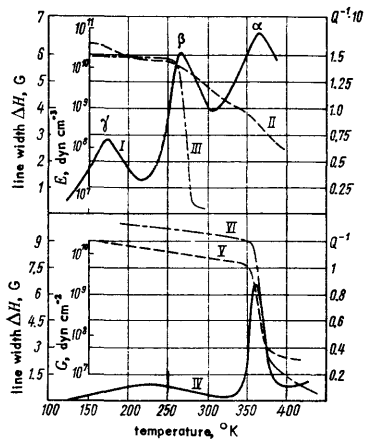


Fig. 11. Temperature dependence of the internal friction (curves I and IV), modulus of elasticity E (curve II), absorption line width (curves III and VI), and modulus of shear G (curve V) of high-pressure polyethylene (a) and poly(vinyl chloride) (b): I) and II) $\nu \sim 10^3$ c/s; IV) and V) $\nu \sim 1$ c/s.

that the agreement between the transition temperatures measured by the NMR and internal friction methods probably cannot be regarded as proof that the same molecular mechanism operates in both cases. It is difficult to imagine the existence of any close relation between molecular motions responsible for the Q^{-1} maximum, which occurs in poly(vinyl chloride) at 330°K and frequencies of the order of 1 c/s, and the motion responsible for the narrowing of the NMR line, which occurs in the same temperature range but at magnetic field frequencies of the order of 10^5 c/s §. Nevertheless the above correspondence between the transitions is observed very frequently [194,195] and therefore there is no reason to believe that this correlation is fortuitous.

A second broad maximum is clearly seen on the Q^{-1}–T curve for poly(vinyl chloride) at about 240°K. It also exists on the tan φ_e curve [237]. However, in the region of this temperature there are no significant changes in the NMR line width. This second Q^{-1} maximum is probably due to slight vibration of methylene groups in the main chain [194].

Fig. 11a shows that the appearance of the low-temperature internal friction maximum (γ-peak) is not accompanied by a sharp change in the width of the NMR resonance line. But the second maximum (β-peak) is satisfactorily correlated with the change in the width of the absorption line. The transition at about 265°K was first observed by the internal friction method [104,114,117,230], but its nature was elucidated by the NMR method. It is due to the rotation of CH_2 side-groups.

Comparison of the second moment of the absorption line with internal friction data suggests that the γ-peak is due to a reorientation of CH_2 groups [108,194]. It has also been suggested [238] that the γ-peak is due to a change in the nature of stereoregularity as a result of cooperative *trans–cis* transitions in polymeric chains. The high-temperature Q^{-1} maximum (α-peak) was discussed above. It is associated with the transition from the state where the main chain is "frozen" to one where its deformation is possible. The corresponding narrowing of the NMR line is almost imperceptible [194]. The study of molecular motion in polymers at these temperatures is best made with the aid of the internal friction and dielectric loss methods. The internal friction method is also preferable in the observation of secondary transitions in the amorphous regions, associated with the motion of individual atomic groups, for example low-temperature transitions in polymers [49,55,104,106,111,125,128,169-171,202].

§ For a more detailed discussion, see Ref. 236.

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All this puts great responsibility on chemists, who are armed with modern methods of investigation and the resolve to make a worthwhile contribution to the common task of building a communist society.

Extensive development of theoretical research in all areas of chemistry and a strengthening of the links with industry—these are the most important aims put before Soviet scientists by the XXIIIth Congress of the Communist Party of the Soviet Union, goals which will doubtless be achieved. The remarkable achievements of Soviet chemistry during the fifty years of Soviet rule are a guarantee of this.

U.D.C. 546

FIFTY YEARS OF DEVELOPMENT OF INORGANIC CHEMISTRY IN THE SOVIET UNION

V.I.Spitsyn

The Great October Socialist Revolution opened up unprecedented possibilities for the development of science in the Soviet Union. In fifty years, an extensive network of research centres has been created, and large numbers of teams of highly qualified specialists have been educated and trained for these centres. Considerable success has been achieved in the planned development of science and in the coordination of its various branches.

The intensive growth of theoretical and applied studies, together with the general sharp increase in the industrial potential of the country, has created favourable conditions for the development of strong Soviet research schools, many of which have now obtained world recognition.

It was the creation of a strong science-backed industrial basis for the new technology in the Soviet Union that enabled the country to withstand the severe trials of the Great Patriotic War against German fascism. The same factors in the post-war years made it possible in a short time to resolve such complex problems as the creation of an atomic industry and nuclear energy, the construction of powerful rockets and the development of propellants for them, the organisation of the production of semiconductor and laser materials, etc. Here an important part has been played by the chemical sciences, and by inorganic chemistry in particular.

Inorganic chemistry originated in Russia two hundred years ago when M. V. Lomonosov carried out studies of the oxidation of metals, of outstanding scientific importance, and for the first time on the basis of experimental data formulated the law of conservation of matter. In 1869, D. I. Mendeleev made an outstanding contribution to the development of world science by his discovery of the Periodic Law governing the chemical elements; this law represents the greatest generalisation of our knowledge in the field of inorganic chemistry. The Periodic Law formed the basis for the development of subsequent work involving the study of atomic structure, the phenomena of radioactivity, and the synthesis of new chemical elements.

Scientists in Russia developed the theory of solutions and carried out studies of the platinum metals, one result of which was the discovery of the element ruthenium. Silicates, peroxides, salt ammines, crystal hydrates, and the radioactive elements were studied. The foundations were laid for the development of the method of physicochemical analysis, which has given particularly valuable results in the study of alloys and intermetallic compounds.

Despite the high scientific level of this work, however, the total volume of research on inorganic chemistry in Russia before the revolution was clearly inadequate and the studies were carried out in only a few places: the chemical laboratory of the Academy of Sciences and the inorganic chemistry departments of the universities and certain higher educational establishments of other types. The grants made by the Tsarist government to the maintenance of these laboratories were negligible. There were no specialised research institutes. The number of inorganic chemists carrying out scientific research work throughout the whole of Russia did not exceed several dozen.

Decisive changes in the development of inorganic chemistry and the whole of science took place after the Great October Socialist Revolution. In Soviet Russia, among other measures designed to strengthen science, a start was made in the organisation of chemical scientific research institutes. In 1918 the Institute of Physicochemical Analysis and Institute for the Study of Platinum and Other Noble Metals were founded in the Academy of Sciences. The Central Laboratory founded by the Higher National Economic Council subsequently became the Karpov Physicochemical Institute. The Scientific Institute for Fertilisers, State Applied Chemistry Institute, the Institute for Pure Reagents, the Radium Institute, and a whole series of other research establishments were organised. Scientific research work was extended in the inorganic chemistry departments of Moscow and Leningrad universities and many other higher educational establishments. An important centre for the development of Soviet inorganic chemistry was provided by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, formed in 1934.

On the instructions of the government, the scientific research institutes and the departments of the higher educational establishments carried out extensive studies of native raw materials and methods for processing them, and helped industry to organise various new production systems, ensuring the economic independence of the young Soviet republic. The rare chemical elements were studied, and on the basis of the scientific research work which was carried out, industry organised the production of many rare metals and their compounds. Scientific research establishments were provided with pure chemical reagents, prepared in Soviet factories.

Since the time of the first five-year plans for the development of the national economy of the USSR (the years 1929–1932 and 1933–1937), the work of Soviet research chemists has been directed chiefly towards the provision of direct assistance in the task of socialist construction. In this period, inorganic chemists have developed the scientific basis for many technological processes in the chemical industry, metallurgy, and the production of binding agents.

Under the direction of N. S. Kurnakov, the salt reserves of the Soviet Union were explored, salt deposits and salt lakes were studied, and methods of natural salt technology were developed. Of particular importance was the study of the Kara-Bogaz-Gol bay in the Caspian Sea, leading to the

organisation of the industrial utilisation of its vast reserves of mirabilite. At the same time, studies were carried out on the dehydration of Glauber's salt and methods for converting it into other compounds.

Thanks to the work of N. S. Kurnakov and his coworkers, vast deposits of potassium minerals were discovered in the USSR, first around Solikamsk, and later in the Ural-Emba region of Western Kazakhstan. Studies were carried out to develop the technology of the natural potassium salts carnallite and sylvinite. In recent years the discovery of vast reserves of potassium salts in Belorussia and the construction of factories for the processing of these salts has strengthened even further the raw-material and technical basis of the Soviet potash industry.

As a result of this scientific research work and the detailed study of natural raw materials containing sodium and potassium, the Soviet Union is assured of a complete supply of compounds of these elements. Instead of importing potassium fertilisers from abroad, as was done before the revolution, the Soviet Union is now able to export these materials. At the same time the country has been provided with magnesium compounds, which have served as raw material for the production of metallic magnesium and various magnesium-containing constructional materials.

The electrochemical preparation of magnesium was studied by V. P. Il'inskii and P. F. Antipin. Studies were made of the dehydration of magnesium chloride hexahydrate, used as electrolyte for the isolation of metallic magnesium. The results of these studies provided information for the construction of magnesium factories.

In the period of industrialisation in the USSR, one of the most important technical problems was the organisation of the production of metallic aluminium from native raw material. Before the discovery of the high-grade Urals bauxites on the eve of the Second World War, the Soviet aluminium industry was based on the comparatively poor Tikhvin bauxites.

In the period 1926–1932, under the direction of A. A. Yakovkin, a large group of research workers developed methods of bauxite technology involving sintering with chalk and soda. The concentrated material was subjected to hydrometallurgical processing. As a result, the problem of the industrial utilisation of high-silica bauxites was solved successfully for the first time. Yakovkin's method was applied in the first factories of the Soviet aluminium industry—the Volkhov Aluminium Combine.

A. N. Kuznetsov and E. N. Zhukovskii put forward another method for the processing of low-grade aluminium ores, involving the high-temperature treatment of a mixture of bauxite, scrap iron, anthracite, and barium compounds. The resulting barium aluminate slag was used for the isolation of alumina. The ferrosilicon formed during the smelting is used in ferrous metallurgy. This method was introduced in the Dnepr aluminium factory.

Under the direction of P. P. Fedot'ev, the electrolysis of cryolite–alumina melts was studied, a new theory of the electrolysis of alumina was developed, and methods for the electrolytic production of aluminium under industrial conditions were devised. On the basis of this work, starting in 1932, Soviet aluminium production was organised, rapidly reaching considerable dimensions, and providing qualified personnel for the further development of this extremely important branch of industry.

Considerable work was done on the search for new forms of cement. P. P. Budnikov studied important problems related to the phenomena of dehydration, hydration, dissolution, and recrystallisation of calcium sulphate. He suggested the use of additives which could "vitalise" insoluble natural anhydrite or gypsum which had been heated at 600–750°C. On the basis of these studies, Budnikov developed a new form of binding agent—anhydrite cement—which has been widely used in constructional work. Budnikov also studied the reactions taking place during the setting of alumina cement and put forward a new form of this material—alumina cement containing added gypsum. This cement is of considerable practical importance.

Later, P. A. Rebinder, N. V. Mikhailov, and others, on the basis of the application of the methods of physicochemical mechanics to the processes involved in the setting and hardening of cements, proposed new forms of constructional materials—sand concrete and colloidal cement binding agent.

Extensive work was carried out in the Soviet Union on the chemistry and technology of phosphorus compounds. The vast deposits of apatite discovered in 1926 in the Kola peninsula were received with mistrust by Soviet industry, since the usual methods for the conversion of natural phosphates into phosphorus fertilisers proved to be inapplicable to these materials. Foreign firms, to whom specimens of the apatite ore were sent for experimental processing, rejected this form of raw material. Studies carried out under the direction of S. I. Vol'fkovich in the Scientific Institute for Fertilisers, however, established the optimal conditions for the conversion of the apatites into phosphorus fertilisers, and the Soviet Union is now assured of an unlimited supply of raw material for the production of these fertilisers, which are of the greatest importance for agriculture.

Studies were also carried out on the chemistry and technology of the rare elements.

One of the first tasks with which the Academy of Sciences was faced was the development of a method for the extraction of radium from native uranium–vanadium ores. This difficult task was successfully resolved under the direction of V. G. Khlopin, and in 1921 the workers of the Radium Experimental Factory produced a specimen of radium bromide—the first fruits of the Soviet rare elements industry. Several years later, the production of pure uranium compounds was organised in the USSR on the basis of the same raw material.

In 1922, studies on the chemistry and technology of tungsten and molybdenum were begun in the Inorganic Chemistry Laboratory of Moscow University. Some years later, this work, which was carried out by T. M. Serbin, G. A. Meerson, V. I. Spitsyn, and others, led to the organisation of tungsten and molybdenum wire production for the electric lamp industry. The creation of a basis for refractory rare metals production led subsequently to the manufacture of hard alloys based on tungsten carbide and to the preparation of other compounds of tungsten. G. A. Meerson, I. A. Shlygin, and other workers from the Moscow Electrical Factory also worked on problems associated with the production of metallic niobium and tantalum.

Under the direction of E. V. Britske, I. V. Shmanenkov, and K. Kh. Tagirov, important work was carried out in the Applied Mineralogy Institute on the utilisation of Urals titanomagnetites. This form of raw material, which is widely distributed in the Urals, cannot be subjected to ordi-

nary metallurgical processing because of its high titanium content, which leads to the formation of refractory slags in the blast furnace. At the same time, valuable amounts of vanadium were discovered in the titanomagnetites. This group of research workers proposed smelting the titanium magnetites in the blast furnace with the addition of rock salt, to give more fusible calcium sodium titanium slags and vanadium-containing cast iron. A method was developed for the conversion of the titanium slags into titanium dioxide.

M. P. Pavlov proposed another method for the processing of titanomagnetites, involving blast-furnace smelting with the use of dolomite as a flux; this also makes it possible to lower the melting point of the titanium slags and to obtain vanadium-containing cast iron. Thus the problem of the processing of titanomagnetite ores was solved completely by the persistent efforts of Soviet research scientists.

M. N. Sobolev, K. A. Bol'shakov, and N. V Krasil'nikov put forward a method, based on laboratory and pilot-plant studies, for the extraction of vanadium from the waste products obtained in the processing of vanadium-containing cast iron. The factory which was built for the production of vanadium compounds played an important role during the Great Patriotic War of 1941–1945, since it provided a complete supply of ferrovanadium for Soviet high-grade metallurgy.

Considerable work was also carried out on other, even rarer elements. Studies by E. S. Burkser and his coworkers in the Ukrainian SSR were directed towards the development of the technology of lithium, ribidium, and caesium compounds and ensured the supply of these elements.

V. I. Spitsyn and G. F. Silina in 1932 developed a method for the production of metallic beryllium and its compounds from natural raw material and organised the industrial production of beryllium.

A series of studies on the chemistry of the rare-earth elements was carried out by I. N. Zaozerskii, D. I. Ryabchikov, and others, and these permitted the production of compounds of these elements under industrial conditions.

O. A. Suvorov and his coworkers in the Kazakh SSR carried out a series of studies on the chemistry of rhenium, and this made possible the production of this metal from the waste products from the Balkhash copper smelting plant.

Work carried out in the USSR on the chemistry and technology of bromine and iodine led to the production of these elements from petroleum drilling waters on a scale sufficient to satisfy the requirements of the Soviet Union.

Outstanding studies of the chemistry of the platinum metals were carried out by L. A. Chugaev, I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, N. K. Pshenitsyn, and their coworkers.

L. A. Chugaev prepared a whole series of representatives of a new type of complex compound of quadrivalent platinum—its amido-derivatives. He worked on the hydrazine and hydroxylamine compounds of platinum, the study of which was later developed by his pupils. Chugaev also studied the physicochemical properties of the ammine complexes formed by platinum(II) nitrite and prepared the previously unknown chloropentammine.

L. A. Chugaev died very early (1922), before reaching the age of fifty. His outstanding achievement was the foundation of a research school which has carried out extremely interesting studies in the chemistry of platinum and the elements accompanying it.

Chugaev's pupil I. I. Chernyaev in 1925 discovered the "trans effect"—the most important theoretical generalisation in the chemistry of complex compounds in the last fifty years. Chernyaev established that in complexes with a square or octahedral structure the strength of the bond formed by a given ligand with the central atom depends on the nature of the ligand in the *trans*-position. This influences its replacement by other ions or molecules which are less influenced by the trans effect.

For example, a strong trans effect is shown by the nitro-group NO_2. In a study of hydroxylamine derivatives of platinum(II), Chernyaev established that in the compound

$$\begin{matrix} Cl\ NH_3 \\ Pt \\ NH_2OH\ NO_2 \end{matrix}$$

the chlorine atom in the *trans*-position relative to the nitro-group is particularly readily replaced by various radicals and neutral molecules, for example, ammonia or pyridine. In *cis*-chloronitrodiammineplatinum(II), the ammonia in the *trans*-position relative to the nitro-group is labile, whereas in *trans*-chloronitrodiammineplatinum(II) the chlorine atom is labile. The reactions with silver nitrate indicate that in the *cis*-compound the chlorine is attached by a covalent bond, whereas in the *trans*-compound the chlorine is ionic.

Atoms and molecules can be arranged in the following order of decreasing trans effect: R_2S, NO_2^-, SCN^-, I^-, Br^-, Cl^-, F^-, OH^-, ..., RNH_2, NH_3, H_2O.

A. D. Gel'man discovered that unsaturated organic molecules such as ethylene and acetylene have a large trans effect.

The systematic occurrence of the trans effect, discovered in platinum(II) compounds, was subsequently applied successfuly to compounds of platinum(IV), palladium(II), rhodium(III), iridium(III), and cobalt(III), and various other elements.

The systematic occurrence of the trans effect makes it possible to predict the direction of reactions in the inner sphere of coordination compounds. It has therefore played an outstanding part in the development of methods for the preparation of new complex compounds. As an example, mention may be made of the work of I. I. Chernyaev and O. N. Andrianova on the preparation of the geometric isomers of the triamine $[PtBrCl(NO_2)(NH_3)En]Cl$. This complicated task was completed with the preparation of three new compounds of the six predicted by theory. The preparations involved a large number of stages and were entirely based on the use of the systematic occurrence of the trans effect.

The phenomenon of the trans effect makes it possible to develop further the ideas of A. M. Butlerov and V. V. Markovnikov on the mutual chemical influence of atoms in the same molecule. The remarkable feature of the phenomenon discovered by I. I. Chernyaev is that it is shown not by neighbouring atoms, but by ligands separated by a central atom.

B. V. Nekrasov put forward a theoretical explanation for the trans effect based on the characteristic deformability of the complex-forming atom. According to his views, the nature of the trans effect is close to the effect of ion counter-polarisation. A. A. Grinberg calculated theoretically the decrease in the strength of attraction between the

platinum(II) ion and the chloride ion, which should be observed when a second chloride ion is attached in the *trans*-position relative to the first, and showed that this effect is sufficient to produce the trans effect. Thus the trans activity of a ligand is determined by the energy of the mutual polarisation of the ligand and the central atom.

In addition to this work, a large number of mixed hexammine, pentammine, tetrammine, and triammine complexes of platinum(IV) were prepared and studied (I.I. Chernyaev and coworkers). Complexes of platinum with organic substances —pyridine, nitriles, isonitriles, etc.—were prepared.

A.D. Gel'man and L.N. Essen prepared for the first time a complex of platinum(IV) with six different inner-sphere substituents.

V.V. Lebedinskii prepared the previously unknown mono-, di-, tri-, and tetra-ammine complexes of rhodium(III), and also compounds of rhodium with thiourea. A.A. Grinberg prepared derivatives of palladium monoammines, and V.I. Goremykin prepared compounds of palladium containing hydrazine and hydroxylamine. New compounds of iridium, with thiourea in particular, were prepared. O.E. Zvyagintsev and his coworkers prepared nitrosonitrato-compounds of rutheium(II). It was shown that ruthenium is not precipitated from solutions of these substances by various reagents, which readily precipitate it from other compounds. A.M. Rubinshtein carried out extensive studies on the preparation of spectroscopically pure specimens of platinum and some of the metals accompanying it.

A.A. Grinberg and his coworkers made extensive studies of the acid–base and redox properties of complex compounds. Measurement of the dissociation constants showed that as a result of the conversion of the NH_3 molecule into the NH_2 amido-group, the ammines of platinum(IV) act as weak acids. The amidoammine complexes of platinum undergo the opposite reaction and exhibit weakly basic properties upon reaction with water.

It was found that the redox properties of ionic complexes depend not only on the nature of the central atom but also to a particularly marked extent on the nature of the ligands in the inner sphere. The appreciable lability of the inner-sphere substituents in compounds such as $K_2[PtBr_4]$, $K_2[PtBr_6]$, $[PtBr_2(NH_3)_4]$, and various others was proved by A.A. Grinberg and F.M. Filinov by isotopic exchange with radioactive tracers. On the other hand, the central atoms of the compounds studied underwent almost no isotopic exchange with corresponding ions from the solution. On the basis of this work, new analytical methods were proposed for the determination of iridium and platinum.

As a result of these studies, thousands of new compounds of the platinum metals were obtained and original methods for their preparation were developed. The development of the chemistry of the platinum metals led to improved methods for the separation and purification of these elements. Before the Great October Socialist Revolution a considerable quantity of platinum-containing raw material was mined in Russia, but the industrial refinement of platinum and the metals accompanying it were not carried out. From the work of the Chugaev–Chernyaev research school, a platinum industry was created in the USSR, producing from native raw materials all the platinum metals in a high state of purity.

A considerable amount of work on the chemistry of complexes was carried out by Ya.A Fialkov and his coworkers in the Academy of Sciences of the Ukrainian SSR. The materials studied were chiefly coordination compounds in which the central atom is non-metallic—polyhalides, polysulphides, double halides of phosphorus, antimony, and other elements, derivatives of iodine halides with organic substances, etc. A new type of complex containing iodine as cation was discovered. In the study of phosphorus halides, the existence of the tetra-acido-cations $[PCl_4]^+$ and $[PBr_4]^+$ was proved for the first time.

Systematic studies in the thermochemistry of complexes have been carried out since 1946 by K.B. Yatsimirskii and his coworkers. The heats of formation of complexes of cobalt, nickel, copper, zinc, and other transition metals (ammine, ethylenediamine, pyrophosphato-, and oxalato-complexes, etc.) have been determined. Kapustinskii's equation and other generalisations have been used to calculate for the first time the heats of formation of gaseous complex species from the gaseous components (central atom and ligands). K.B. Yatsimirskii then realised the transition from thermochemistry to the complete thermodynamic characteristics of reactions involving complex formation (the changes in enthalpy, entropy, and free energy). New methods were put forward for studying the complex formation equilibria. These include a spectrophotometric method for solutions in which several coloured complexes exist together. A kinetic method for studying the equilibria has been developed, based on the change in catalytic activities on complex formation. New methods for the mathematical treatment of data on equilibria have been proposed. A large number of equilibria in solutions of complex compounds have been studied experimentally.

There has recently been an extensive development of studies of electronic spectra and their application to the investigation of the characteristic features of the structures of complex compounds (the symmetry of the inner sphere, chemical bonding, and the fine details of the structure of the inner sphere). These methods have been applied to the complex compounds of the rare-earth elements by K.B. Yatsimirskii, N.K. Davidenko, and N.A. Kostromina. The interpretation, correlation, and generalisation of the thermodynamic, kinetic, and optical characteristics of complex compounds have been carried out on the basis of modern theoretical concepts (crystal field theory, the method of molecular orbitals, etc.).

Studies of considerable scientific value have been carried out in the chemistry of radioactive elements by V.G. Khlopin and his pupils. Khlopin's work involved chiefly the study of the laws governing the coprecipitation of radioactive elements, present in solutions at extremely high dilutions, with crystalline or amorphous precipitates separating from the solutions. Khlopin established that entrainment of the radioactive element by the crystalline precipitate takes place only if its compound is isomorphous with the substance being precipitated. The micro-component is then distributed between the crystals and the solution as a dissolved substance is distributed between two immiscible solvents. An important part is played by recrystallisation of the solid phase to achieve homogeneity and to establish equilibrium in the system with respect to the macro-component. The study of more than thirty systems containing radium, polonium, radium-D (a lead isotope), and other radioactive elements as micro-components showed that the distribution law was obeyed rigorously. Salts of barium, lead, uranium, cerium, etc. were used as the macro-component.

The Soviet radium industry has made extensive use of the practical results of the research work of Khlopin's

school. Methods for separating radium and barium have been improved considerably and new methods have been developed in the technology of radioactive substances.

This work has also led to the following conclusion: the applicability of Khlopin's law to the distribution of a micro-component in a system containing crystals and a solution of a macro-component proves that in the given instance the micro-component is isomorphous with the macro-component and replaces it in the crystal lattice. The use of radioactive tracers has thus opened up new methods for the study of the phenomena of isomorphism.

In particular, this method can be used to establish the existence of unstable compounds or compounds present in negligibly small quantities, and to study their composition and structures. In this way, V.G.Khlopin and A.G.Samartseva established that polonium forms bivalent compounds which cocrystallise with sodium telluride Na_2Te. In an oxidising medium, cocrystallisation with lead tellurate $PbTeO_4$ revealed the existence of polonate ions, corresponding to the previously unknown sexivalent polonium.

The method of "isomorphous cocrystallisation" using radioactive tracers was used by V.G.Khlopin and B.A.Nikitin to study the phenomena of so-called second-order isomorphism, in which isomorphous replacement takes place when the substances have structures of the same chemical type, irrespective of any chemical analogy. Examples include the isomorphism of barium sulphate and potassium permanganate ($BaSO_4$, $KMnO_4$), barium chromate and potassium tetrafluoroborate ($BaCrO_4$, KBF_4), sodium bromide and lead sulphide (NaBr, PbS), etc. For the example of systems containing rubidium perchlorate and radium sulphate ($RbClO_4$, $BaSO_4$), Khlopin and Nikitin showed that at concentrations of about 10^{-6}% lead and radium do not enter the crystal lattice of the perchlorates. This established the existence of a lower miscibility limit for second-order isomorphous replacement. At the same time the perchlorates studied could entrain radium or lead sulphates if the latter were present in concentrations sufficient for the construction of their own crystal lattice. This leads to a conclusion of considerable scientific importance: in true isomorphism, replacement takes place ion for ion, atom for atom, or molecule for molecule; in second-order isomorphism, however, the replacement involves complete sections of the crystal lattice, with dimensions varying from one unit cell to a comparatively large number of unit cells.

B.A.Nikitin used the principle of isomorphous cocrystallisation to study possible compounds of the inert gases. He established that sulphur dioxide hydrate $SO_2.6H_2O$, below its eutectic point (−2.6°C) absorbs radon even at a negligibly low concentration of the latter. The process obeys the distribution law. This proved that radon forms a hydrate isomorphous with the hydrate of sulphur dioxide, with composition corresponding to the formula $Rn.6H_2O$.

An analogous phenomenon was observed for other inert gases—argon and neon. The distribution constants between the gaseous phase and the solid hydrate $SO_2.6H_2O$ were different for the inert gases studied. By carrying out the separation of the sulphur dioxide hydrate in several stages and controlling the temperature, it was found possible to achieve the fractional separation of the inert gases by this chemical method.

Subsequently, B.A.Nikitin demonstrated in analogous fashion the existence of compounds of the inert gases with toluene, phenol, and *para*-chlorophenol, for example, $Rn.2C_6H_5CH_3$, $Rn.3C_6H_5OH$, and $Rn.3ClC_6H_4OH$. The molecular compounds $HBr.2C_6H_5CH_3$, $H_2S.3C_6H_5OH$, $H_2S.3ClC_6H_4OH$, etc. were used as carriers. In this way it was established that the ability of inert gases to undergo chemical reaction is not restricted to the formation of hydrates, but also extends to many organic compounds. B.A.Nikitin considered that the stability of the compounds of the inert gases which he obtained approaches that of molecular compounds. The atoms of the inert gases behave as the molecules of chemical compounds.

One of the most important ways of increasing the efficiency of the separation of elements by cocrystallisation involves the use of complex-forming reagents. This approach, pointed out by V.G.Khlopin, was developed by N.B.Mikheev and L.M.Mikheeva, who put forward equations which make it possible to calculate the degree of separation of elements under conditions of equilibrium and non-equilibrium cocrystallisation. It was shown that electrically neutral complexes can take part to only a slight extent in the cocrystallisation of ionic salts. These studies represent an extension of the thermodynamic theory of cocrystallisation, developed by A.P.Ratner, a pupil of V.G.Khlopin.

The difficulty of attaining equilibrium between mixed crystals and solution presents an obstacle to the development of multiplicative schemes for the separation of elements. V.I.Spitsyn, N.B.Mikheev, and A.Khermann developed an electrochemical method for the forced recrystallisation of sparingly soluble salts and achieved the "elution" of impurities cocrystallising with the precipitate.

The theoretical principles of the processes of ion adsorption on precipitates were developed by A.P.Ratner and V.G.Khlopin, together with V.I.Grebenshchikova and M.S.Merkulova.

M.S.Merkulova and I.V.Melikhov have recently studied non-equilibrium cocrystallisation, which is often encountered in practice. They distinguish the various stages which may limit the process, depending on the conditions of cocrystallisation.

V.I.Spitsyn and V.V.Gromov established that radioactive irradiation of the specimens influences the cocrystallisation. High radioactivity in the precipitate leads to more intensive recrystallisation, and this increases the rate of attainment of equilibrium in the system.

In addition to the study of cocrystallisation processes, studies have been made of the application of various forms of ion-exchange adsorption to the separation of radioactive elements.

Using various sorbents (glass, activated carbon, ion-exchange resins, etc.), I.E.Starik determined the state of various multivalent elements in dilute solutions.

B.P.Nikol'skii and V.I.Paramonova used the method of ion exchange to study the composition and stability of complexes of radioactive elements and isotopes. Their studies were among the first in this field.

V.I.Spitsyn and V.V.Gromov showed that the radioactive irradiation of precipitates influences their sorptive properties. The magnitude of the adsorption of basic and acidic dyes on a barium sulphate precipitate containing radium or the radioactive tracer ^{35}S, depends on the magnitude and nature of the radioactive irradiation of the isotope present; this is directly related to the electric charges produced on the surface of the solid phase, depending on whether alpha- or beta-particles are emitted.

The considerable progress made in the development of the theory of cocrystallisation and adsorption processes has found extensive technological application in the preparation of radioactive isotopes.

Soviet scientists have carried out a considerable amount of experimental and theoretical studies, covering the chemistry of the elements of all groups of the Periodic System. Only some of these can be mentioned in this brief review.

The systematic study of metal hydrides in the Soviet Union was begun by I. I. Zhukov, who showed that they can be divided into several classes—individual chemical compounds and solid solutions of hydrogen in the metals or the individual hydrides.

The preparation of the hydrides of various refractory rare metals (titanium, vanadium, niobium, and tantalum) by the reaction of the oxide of the corresponding element with calcium hydride at an elevated temperature was studied by G. A. Meerson and his coworkers.

I. A Kazarnovskii and his coworkers, on the basis of a study of the hydrides of the alkali and alkaline earth elements, calculated the radius of the negative hydrogen ion and the electron affinity of the hydrogen atom.

The hydrides of boron and the hydrides of the light and transition metals have been studied since the early nineteen-fifties by V. I. Mikheeva and her coworkers. Stable molecular compounds of diborane with pyridine, aniline, and other amines have been prepared. Optimal conditions have been established for the preparation of the alkali metal and magnesium hydrides, and also hydride halides of the type MgClH, etc. A method has been developed for the preparation of the complex tetrahydroborates and tetrahydroaluminates of various metals by double decomposition in aqueous or organic solutions, and also in salt melts. The tetrahydroborates of calcium, magnesium, and aluminium, and the tetrahydroaluminates of magnesium, cerium, and other metals have been prepared in this way.

Soon after the discovery of the heavy isotope of hydrogen, studies using deuterium were carried out in the Ukraine by A. I. Brodskii, who organised the laboratory production of heavy water as early as 1934. Brodskii and his coworkers developed an interferometric method for the quantitative determination of deuterium and carried out a number of extremely interesting studies of the isotopic exchange of hydrogen in various inorganic and organic compounds. A. I. Shatenshtein developed methods for the preparation of many deuterium compounds and carried out extensive studies of hydrogen exchange in non-aqueous solvents between various classes of substance, using their deuterium derivatives.

In the field of the rare alkali metals, mention must be made of the work of V. E. Plyushchev, who proposed new methods for the extraction of lithium and caesium from natural raw material. The study of polyhalides and double compounds with the chlorides of antimony, bismuth, and tin made it possible to improve methods for the separation of rubidium and caesium. Solid-phase reactions were used to prepare mixed compounds of rubidium, caesium, and the rare-earth elements—various zirconates, niobates, tantalates, etc.

The chemistry of beryllium has developed considerably. A. V. Novoselova, O. I. Vorob'eva, K. N. Semenenko, and others have synthesised a whole series of new fluoro-complexes of beryllium and have established the physicochemical conditions of their formation. Previously unknown crystalline modifications of beryllium fluoride, sodium fluoroberyllate, and other compounds have been discovered. New data have been obtained on the structural and chemical analogies between the fluoroberyllates and sulphates of the alkali and alkaline earth elements.

The same research team has studied the properties of beryllium nitrate and sulphate—the composition of the crystal hydrates, the thermal stability of the compounds, etc. Various covalent beryllium compounds have been prepared, and their properties and structures have been studied: these include oxide salts—the oxide formate, oxide acetate, oxide propionate, and oxide benzoate—and their compounds with various organic and inorganic molecules, alkoxy-derivatives, and compounds with ammonia and amines, nitrogen dioxide, and sulphur dioxide. Studies have been made of the properties and structures of the compounds formed by beryllium chloride with various inorganic and organic molecules, and the nature of their reactions in non-aqueous solvents.

In an investigation of natural brines containing boron, A. V. Nikolaev made a detailed study of calcium, magnesium, sodium, and potassium borates, and discovered an extremely interesting phenomenon, which has been described as borate rearrangement: when a hydrated borate is heated, the endothermic dehydration is followed by a clearly defined exothermic effect, which causes the temperature of the borate to rise spontaneously to a value which is 50–100 deg higher than the temperature of the heater. The borate rearrangement results from the crystallisation of the amorphous anhydrous borate formed initially.

B. N. Ivanov-Emin and his coworkers have carried out interesting studies on the amphoteric properties of the elements of the gallium subgroup. Acidic properties are observed in the oxides of all elements of this subgroup, but the acidity decreases sharply in the order gallium–indium–thallium, corresponding to the rules which follow from D. I. Mendeleev's Periodic Law. Sodium hexahydroxoindate $Na_3[In(OH)_6].2H_2O$, which is stable only in strongly alkaline medium, was prepared for the first time.

E. N. Deichman carried out a number of studies on the chemistry of simple and complex compounds of indium. She prepared hydrogen sulphatoindates—$H_3In(SO_4)_3$ and others—and prepared sulphato-, oxalato-, mixed sulphato-oxalato-, fluorosulphato-, and phosphato-compounds of indium. In the pre-revolutionary period, outstanding studies on the chemistry of the rare-earth elements were carried out by the Russian chemist N. A. Orlov. His last work, concerned with the isolation, by fractional crystallisation, of specimens of the least readily accessible elements of this group—holmium, dysprosium, and others—was published in the Soviet period.

Scientific research work on the rare-earth elements in the Soviet Union was held up for a considerable time by the lack of suitable raw material for their extraction. In the nineteen-thirties, considerable attention was drawn to the rare-earth minerals of the Kola peninsula, particularly lovchorrite—a titanofluorosilicate of calcium and the rare-earth elements. I. N. Zaozerskii and P. I. Protserov put forward an acidic method for its decomposition, and E. S. Burkser and G. P. Aleksandrov put forward a chlorination method. These gave the first Soviet specimens of the rare earths.

During the period of industrialisation, Soviet industry began to make extensive use of Khibiny apatites as raw

material for the production of superphosphate. The apatite concentrate contains more than 1% of rare earths of the cerium group, and this is of considerable interest in view of the large scale of phosphorus fertiliser production. S.I. Vol'fkovich and A.I. Loginova put forward a method for the extraction of rare earths from apatite during its acid conversion into concentrated fertilisers. A rare earth concentrate can be isolated by fractional precipitation from the solution using lime.

The production of compounds of the rare-earth elements permitted their study and a start to be made in their practical application. D.I Ryabchikov and E.A. Terent'eva studied complexes of the rare-earth elements with organic acids and amines. The rare-earth element in every instance showed a coordination number equal to six. The most stable compounds were obtained with tricarballylic, aconitic, nitrilotriacetic, and citric acids. Study of the last of these established the composition of the complexes—$M^{I}_{3}[M^{III}(C_6H_5O_7)_2]$, where M^{III} represents the rare-earth element. Complexes of medium stability were obtained with antipyrine, pyramidone, and pyridine as inner-sphere substituents around the rare-earth element. In the lanthanide series, the tendency to form complexes was found to increase with decrease in ionic radius.

Subsequent studies on the separation of the rare-earth elements and the preparation of their compounds in pure form developed in two directions—chromatographic methods and extraction methods. In both, an important part is played by complex formation.

L.I. Martynenko and coworkers were the first to use ethylenediaminetetra-acetic acid as eluant in the ion-exchange chromatography of the rare-earth elements. This method was used to prepare for the first time spectroscopically pure specimens of all the rare-earth elements for research organisations.

To obtain a theoretical basis for the optimal conditions for the ion-exchange separation of mixtures of the rare-earth elements, the same group made a systematic study of the composition and properties of the complexes formed by the lanthanides (Ln) with ethylenediaminetetra-acetic acid, nitrilotriacetic acid, and iminodiacetic acid. It was found that the separation generally involves mixtures of complexes. For example, when ethylenediaminetetra-acetic acid H_4A is used, complexes of the type $[LnA]^-$ and $[Ln_2A]^{2+}$ are formed, and when nitrilotriacetic acid H_3X is used, the complexes $[LnX]$ and $[LnX_2]^{3-}$ are formed. In many instances the difference in the quantities of complexes with different compositions is of greater importance for the chromatographic separation of a given pair of rare-earth elements than the difference in the stabilities of the complexes with a given composition formed by the same pair.

The study of reactions in solid-phase systems at elevated temperatures showed that the oxides of the rare-earth elements can react with the oxides of the alkali and alkaline earth metals to form compounds which are isomorphous with the analogous ferrites. Thus the manifestation of amphoteric character, previously known in this family only for scandium, has now been recognised in all the rare-earth elements (L.I. Martynenko, L.M. Kovba, and others).

L.N. Komissarova and coworkers carried out a series of studies on the chemistry of scandium. The sulphates, nitrates, oxide salts, and complexes of this element were studied. New complexes formed by scandium carbonate were prepared, and also salts of oxyacids of phosphorus in various valency states (phosphites, hypophosphite, and a number of phosphates). The results obtained were used to improve methods for the isolation of scandium from natural raw material.

N.E. Brezhneva, V.I. Levin, G.V. Korpusov, and others studied the regular features of the separation of the rare-earth elements by extraction using organophosphorus compounds. The work was originally carried out in connection with the preparation, in a state of radiochemical and chemical purity, of promethium and the radioactive isotopes of the rare-earth elements present in the waste products from the atomic industry—uranium fission products. At the same time a study was made of the mechanism of the extraction of multivalent ions by organic solvents and a direct relationship was established between the structure of the molecules of the organophosphorus extracting agents and their extracting power. The results obtained have also found application in processes for the separation of the stable rare-earth elements. The introduction of the extraction method of separation permitted the large scale isolation of rare-earth elements, in particular yttrium, with a purity of 99.9999%; this has found industrial application.

Among the inorganic compounds of carbon the carbides are important, many of them so because of their hardness and high melting point.

G.A. Meerson and his coworkers have studied the formation conditions of refractory rare metal carbides. The reduction of the oxides, for example titanium dioxide, by carbon leads to the simultaneous formation, in solid solution, of the compounds TiC, TiO, and TiN (the last of these due to the presence of residual air). The problem of preparing pure carbides is proving extremely difficult. The reduction of titanium dioxide by carbon is facilitated by using an atmosphere of hydrogen. The hydrocarbons formed apparently act as carbon carriers. When the reduction is carried out in a vacuum, a mixture of titanium dioxide and carbon gives a solid solution of metallic titanium in the carbide. It is quite probable that the phenomena observed in the formation of titanium carbide are also shown by other carbides.

In the chemistry of silicon, mention must be made of the outstanding studies of I.V. Grebenshchikov on glasses. It is known that ordinary silicate glasses contain sodium disilicate, which is fairly readily soluble in water, and calcium silicate, which decomposes fairly rapidly under the influence of acids, yet a glass containing these compounds shows an unusually high stability towards water, acids, and other chemical reagents. According to Grebenshchikov's studies, all silicate glasses react extremely vigorously and rapidly (in a period of several seconds) with water with the formation of a thin colloidal film of silicic acid on the surface; this film is produced by hydrolysis of the silicates and it prevents further decomposition of the glass. The thickness of this film has been measured by various methods and the film has been found to be extremely thin (10–60 Å).

On the basis of the properties of the surface film of silicic acid, Grebenshchikov obtained information on the part played by chemical processes in the polishing of glass. It was found that it is not the hardness of glass, but its chemical stability, which primarily influences the rate of grinding and polishing. Change in temperature, the introduction of substances into the solution which are adsorbed by the protective film of silicic acid, and the replacement of water by other liquids all have a marked influence on the

thickness and properties of the protective film, and hence on the process of glass polishing.

A whole range of silicate systems has been subjected to detailed study by modern physical and physicochemical methods. On the basis of the research work carried out under the direction of I. V. Grebenshchikov and N. N. Kachalov, the production of first-class optical glass was organised in the USSR in the late nineteen-twenties.

Recently, N. A. Toropov and his coworkers have studied silicate systems containing the rare earths and other refractory oxides.

A large number of studies have been carried out by E. I. Gladyshevskii and his coworkers on the silicides and germanides of various metals. Studies have been made of binary and ternary systems containing vanadium, chromium, manganese, iron, cobalt, nickel, titanium, the rare-earth elements, and many other metals. It is only in a few instances that the compositions of the compounds obtained are determined directly by the main valencies of the components, and for the most part the compositions are determine by geometric and electrochemical factors and the degree of electron delocalisation. The compounds obtained include La_3Si_2, Lu_5Ge_3, VCoSi, $CaAl_2Si_2$, $Mo_5Co_3Ge_2$, etc. In the formation of silicides and germanides, an important part is played by the formation of covalent Si–Si and Ge–Ge chains.

Work on the chemistry of zirconium and hafnium has continued to develop. L. N. Komissarova, Yu. V. Granovskii, and others have studied the processes involved in the separation of these elements by extraction using tributyl phosphate; methods involving mathematical planning of the experiments were used. In the same laboratory, studies have been made of the solid-phase reactions between hafnium dioxide and oxides of the rare-earth elements.

N. A. Godina and others have studied the reaction of zirconium dioxide with the rare-earth elements and of hafnium dioxide with the alkaline earth elements; this has given more accurate information on the equilibrium diagrams for these systems.

Yu. V. Khodakov has shown experimentally that all previously proposed schemes for the hydration of phosphorus(V) oxide are erroneous, since they do not make allowance for the formation of intermediate products—higher polyphosphoric acids: the tetra-acid $H_6P_4O_{13}$ and the tri-acid $H_5P_3O_{10}$. The mechanism established for the hydration of phosphorus(V) oxide corresponds to the theory of the three-dimensional structure of the anhydrides of the oxo-acids, developed by Yu. V. Khodakov.

A. V. Lapitskii has published a number of studies of the chemistry of niobates and tantalates. In particular, he has made a detailed study of the dependence of the dehydration and thermal stability of these compounds on the nature of the cations present.

There has been a considerable increase in information on peroxo-compounds. I. A. Kazarnovskii and his coworkers have studied a new class of oxygen compound of the alkali metals—ozonides—obtained by the action of ozone on the correspoinding hydroxides. The products of the side-reactions were previously known, but the substances obtained in this instance could be isolated in pure form only because of the original method employed—extraction by liquid ammonia. A detailed chemical study was made of potassium ozonide; its structure was studied by X-ray diffraction and magnetic methods, and its heat of formation was measured. It was shown that the structure of potassium ozonide is given by the formula $K^+O_3^-$. Study of the isotopic exchange of oxygen between KO_3 and water enriched in $H_2{}^{18}O$ gave new data on the reactivity of the free hydroxyl radical. A mechanism for the reaction of ozone with alkalis was proposed on the basis of these studies.

Compounds of sulphur, selenium, and tellurium have been widely studied, since they are of considerable interest as semiconducting materials. A. V. Novoselova and coworkers prepared and studied the electrical properties of the binary and some ternary chalcogenides of titanium, zirconium, vanadium, niobium, tantalum, and other metallic elements. Semiconductors and dielectrics have been found among chalcogenides with general formula $A^{II}B^{IV}C_3^{VI}$. The change from dielectrics to semiconductors is accompanied by a change in structural type. The thermal stabilities of a number of selenides and tellurides have been studied. The equilibrium diagrams of the Ge–S, Ge–Se, and other systems have been obtained in fundamental studies on the preparation of semiconducting compounds.

Important studies on the preparation of various arsenides and antimonides have been carried out by N. A. Goryunova.

In the chemistry of the oxygen compounds of sulphur, mention must be made of the interesting derivatives of sulphamic acid prepared by A. V. Kirsanov: *N*-(chlorosulphonyl)phosphorimidic trichloride $ClSO_2.NPCl_3$, sulphanuryl chloride $(NSOCl)_3$, etc.

V. I. Spitsyn and his coworkers have carried out a number of studies on the chemistry of tungsten and molybdenum. The compositions of the isopolytungstates and isopolymolybdates formed by various metals have been established. Detailed study of the dehydration of many aquopoly- and heteropoly-compounds has shown the important constitutional role played by water in these substances. At the same time the use of tracer atoms has established the high mobility of its molecules in these compounds. Isotopic and ion exchange between the anions of various heteropolyacids has been studied. The simultaneous use of two radioactive tracers (^{32}P and ^{185}W) made it possible to establish, by the self-diffusion method, that the reaction between the anions of two acids capable of forming a heteropolycompound (for example, HPO_4^{2-} and WO_4^{2-}) begins even in the alkaline range and apparently involves hydrogen bonding. A new coordination treatment of the structure of aquopoly- and heteropoly-compounds has been put forward, based on oxonium groups and hydrogen bonding, the molecules of the corresponding acids, for example, H_2MoO_4 and H_2WO_4, being regarded as inner-sphere ligands.

E. A. Nikitina has studied problems associated with the preparation of heteropolycompounds and has proposed a method, which does not involve the use of ether, for preparing molybdophosphoric, molybdosilicic, and tungstophosphoric acids by the direct reaction of the corresponding reagents, for example, phosphoric acid and molybdenum(VI) oxide.

A. I. Kokorin and coworkers have studied tri- and tetraheteropolyacids and have prepared a number of new representatives—vanadomolybdophosphoric, tungstomolybdosilicic, vanadotungstomolybdophosphoric, and other similar acids.

Z. F. Shakhova and R. K. Motorkina have studied heteropolycompounds of germanium and certain rare-earth elements. They showed by various methods that the structures of the reduced and non-reduced forms of tungstogermanic and molybdogermanic acids are identical.

V.I. Spitsyn, V.F. Chuvaev, and V.Ya. Kabanov applied proton magnetic resonance to the problem of the basicity of heteropolyacids. According to the Miolati–Rosenheim theories, the central atom in these acids always has a coordination number of six, so that, for example, a high basicity, equal to seven, was assumed for molybdophosphoric acid: $H_7[P(Mo_2O_7)_6]$. X-Ray diffraction studies by Keggin and others led to the conclusion that the usual coordination number of phosphorus and silicon in heteropolyacids is four. The basicity of the heteropolyacids should then be lower; for example, the formula for molybdophosphoric acid should be $H_3[PO_4(MoO_3)_{12}]$. Chemical studies generally did not confirm the formation of salts with a high degree of substitution. The problem remained open, however.

The method of nuclear magnetic resonance makes it possible to distinguish the states of hydrogen atoms in compounds and to decide whether they correspond to H^+, OH^-, H_3O^+, or H_2O. The use of this method established unambiguously that the number of hydrogen ions in ordinary heteropolyacids corresponds to the low basicity which follows from their X-ray diffraction study. Thus the suggestion that there exist salts of heteropolyacids with a high degree of substitution should be rejected.

Simple and complex fluorides have been studied for a number of years by I.V. Tananaev and his coworkers, who were the first to prepare sodium hydrogen fluoride and lithium hydrogen fluoride. The hydrogen hexafluoroaluminates $AlF_3.3HF.6H_2O$ and $AlF_3.3HF.3H_2O$, previously unknown in the free state, have been prepared; these compounds have been described as cryolitic acids. The same group of workers have studied many double fluorides formed by metals. Natural cryolite has been found to have the composition $11NaF.4AlF_3$, and not $3NaF.AlF_3$, as previously assumed. Interesting data have been obtained on the stepwise electrolytic dissociation of the fluoride of multivalent elements.

I.V. Tananaev and his coworkers have also used various physicochemical methods to study heavy metal hexacyanoferrates(II) and the double salts which they form with alkali metal hexacyanoferrates(II). Double potassium–nickel, potassium–cobalt, caesium–cobalt, and other hexacyanoferrates(II) have been isolated for the first time. The compositions of the double hexacyanoferrates(II) formed by potassium with indium and gallium have been established: $KIn[Fe(CN)_6]$ and $KGa[Fe(CN)_6]$. This type of compound has proved to be characteristic for tervalent metals and is usually formed instead of the normal hexacyanoferrates(II). Analogous results were obtained for lanthanum hexacyanoferrates(II). A hexacyanoferrate(II) method has been proposed for the separation of yttrium from cerium and lanthanum. The use of the radioactive silver tracer ^{110}Ag has made it possible to study the replacement of the alkali and heavy metal in various simple and mixed hexacyanoferrates(II) by silver ions and hence to characterise the relative strengths of the bonds formed by the metals in the outer sphere with the hexacyanoferrate(II) ion.

Mention must also be made of the fact that Soviet inorganic chemists have paid considerable attention to the development of the chemistry of the little-studied radioactive elements. V.I. Spitsyn and A.F. Kuzina developed methods for isolating the long-lived isotope of technetium ^{99}Tc from neutron-irradiated molybdenum. These authors prepared various technetium compounds and studied their properties. In the same laboratory, R.A. D'yachkova studied the isolation of protoactinium from the waste products from the processing of uranium ores and for the first time in the Soviet Union obtained ponderable quantities of this element. The forms in which protoactinium exists in aqueous solutions with different acidities have been studied.

After the organisation of an atomic industry in the USSR, research workers were able to study the chemistry of plutonium and other transuranium elements. V.V. Fomin and coworkers showed that in addition to the fluoride $NaPuF_5$ described in the literature, compounds M_2PuF_6, where M = Na or NH_4, exist. Measurement of the vapour pressure of plutonium tribromide in bromine vapour established the formation of plutonium tetrabromide, unstable at low temperature. A detailed study was made of the decomposition of oxalates of plutonium under the influence of its own radiation, leading to the conversion of the oxalates into carbonates and reduction of plutonium. This change in the specimens readily explains their appreciable solubility in acids after they have been kept for some time. Other simple and complex compounds of plutonium were prepared and studied.

A.D. Gel'man, A.I. Moskvin, V.P. Zaitseva, M.P. Mefod'eva, and others have studied complex formation of neptunium, plutonium, americium, and curium in aqueous solutions with various ligands. The stability constants of the ionic complexes have been determined. The kinetics of the valency changes in neptunium and plutonium in nitric acid solutions have been studied, and the influence of complex formation on the redox reactions of these elements has been investigated.

A large number of simple and complex compounds of neptunium and plutonium have been isolated by these authors and characterised in the solid state. Examples include $M_4Np(C_2O_4)_4.nH_2O$, $NpO_2C_2O_4.3H_2O$, and the plutonium(V) compounds $NH_4PuO_2F_2$, $NH_4PuO_2CO_3.3H_2O$, $NH_4PuO_2HPO_4.4H_2O$, $(NH_4)_2PuO_2(OH)CO_3.nH_2O$, and $NH_4[PuO_2C_2O_4].6H_2O$. Pure concentrated solutions of tervalent uranium have been prepared, and various complex compounds have been isolated in solid form from these solutions.

V.M. Vdovenko and coworkers have made a number of studies of complex formation by uranium and plutonium in connection with methods for their separation by extraction. Nitrato-, sulphato-, chloro-, and other complexes have been studied. Tributyl phosphate, diethyl and dibutyl ethers, and various amines have been used as organic media. The structures of various compounds of uranium and plutonium have been established by infrared spectroscopy and proton magnetic resonance.

A traditional field of Soviet inorganic chemistry is the study of metallic alloys and the chemical compounds which they form.

N.S. Kurnakov, G.G. Urazov, and their coworkers have prepared many new alloys based on magnesium and aluminium, and have established their structures. This has made it possible to organise the production of most important materials for the aviation industry and other branches of the national economy.

Studies of heat-resistant alloys based on iron and chromium, carried out by I.I. Kornilov, have made it possible to produce new and valuable materials for high-temperature technology. V.A. Nemilov has prepared a whole series of palladium alloys which had not been studied before. E.M. Savitskii has studied the properties of alloys based on the rare-earth metals. In connection with problems associated with light alloys, A.V. Novoselova, N.D.

Nagorskaya, and others studied for the first time the equilibrium diagram of the Al–Be–Mg system, and also investigated the nature of crystallisation in beryllium-rich alloys of various systems (Be–Nb and Be–Re).

A series of important studies has been carried out by A. F. Kapustinskii on the dependence of the energetics of chemical reactions on the positions of the elements in the Periodic System. He made a systematic survey of the thermodynamic properties of the sulphides of various metals, and put forward a convenient simplified equation for calculating crystal lattice energy as a function of the valencies and radii of the ions forming it.

A valuable contribution to the thermodynamics of inorganic compounds, particularly the halides and oxides of the rare elements, was made by the work of S. A. Shchukarev.

The theoretical principles of chemical bonding in inorganic compounds has been developed by Ya. K. Syrkin and M. E. Dyatkina. A theory of directed valencies and a theory of the valency states of atoms in molecules have been developed, and the interactions of atoms with electrons have been studied from the viewpoint of quantum mechanics. Systematic studies of the valency states of both transition and non-transition elements have made it possible to reach a number of conclusions of importance for inorganic chemistry. In particular, the electronic structure of the tetrahedral oxoanions of the transition metals has been studied. Quantum-chemical calculations of the energies of inorganic compounds have made it possible to make predictions regarding the covalent character of the bonding in crystals; this is extremely significant for an understanding of the semiconducting properties of various inorganic substances.

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In the fifty years for which the Soviet State has been in existence, inorganic chemistry has grown in the Soviet Union, together with the whole of chemical science. As can be seen from this necessarily brief review, considerable progress has been made in many important fields of the development of modern inorganic chemistry. However, the great task which stands before us—the construction of communism by the first workers' state in the world—is increasing to an even greater extent the need for the extensive utilisation of science as a direct productive force in society. The potential possibilities provided by inorganic chemistry in this respect are unusually great: inorganic polymers, laser crystals, refractory and super-hard materials, materials for superconductivity, and many other valuable materials can be provided only by inorganic chemistry.

Our country's anniversary is inspiring Soviet inorganic chemists to new scientific efforts and achievements!

U. D. C. 547

SOVIET ORGANIC CHEMISTRY AFTER 50 YEARS

N. S. Zefirov

Russian organic chemistry long ago won an honourable place in world science. The names of A. M. Butlerov, V. V. Markovnikov, N. N. Zinin, E. E. Vagner, and N. N. Men'shutkin have acquired a wide repute. Russia had strong chemical schools; in this connection special mention must be made of the Kazan' chemical school, which has produced a great number of brilliant organic chemists, to whom world science must be obliged for the greatest scientific achievements.

Despite this, it has fallen to the Soviet land after half a century to make the most grandiose work on the development of chemical science and industry. Before the revolution chemical science had developed only in individual scientific centres and the number of chemists with higher education amounted to not much more than 1000; the organic chemical industry was practically non-existent.

Fifty years later a powerful chemical industry has been created in our country. In the USSR a series of new means of production—coal tar chemicals, aniline dyes, petrochemical, chemico-pharmaceutical, etc.—have been set up where there was literally an empty place. This enormous construction required great forces in assimilating even the experience gained abroad. In addition our country developed novel solutions for various problems in the construction of a chemical industry. The clearest example is the organisation of the production of synthetic rubber, which was the first in the world.

The rapid development of the organic chemical industry in the USSR was based on the experience and traditions of Russian, and then Soviet, organic chemistry. On the other hand, with the development of the chemical industry, organic chemistry obtained a new firm foundation. After years of Soviet power, having opened wide the doors of educational establishments, there grew up in our land an enormous army of organic chemists. A marked extension of the "geography" of organic chemistry resulted—in addition to Moscow, Leningrad, Kazan', Kiev, Tomsk, Khar'kov, Odessa, and Riga, there are now large scientific centres at Gor'kii, Kuibyshev, Novosibirsk, Irkutsk, Vladivostok, Erevan, Tbilisi, Baku, Tashkent, etc.

It is impossible to list all who took part in this. We will only note that during the years of Soviet power new scientific schools have developed which are of worldwide repute and which determine the development of individual branches of organic chemistry not only in our own country but throughout the world. In this connection mention must be made of the school of N. D. Zelinskii, who tackled many problems of the chemistry of hydrocarbons and organic catalysis; the school of A. E. Favorskii and S. V. Lebedeva, who developed the chemistry of unsaturated aliphatic compounds; the school of A. E. Chichibabin, celebrated for their investigations in the field of heterocyclic compounds; the school of A. N. Nesmayanov, who worked at large classes of organoelemental compounds and moulded this division of organic chemistry into an independent field; the school of A. E. Arbuzov, whose studies in the field of the chemistry of organophosphorus compounds are well known.

The basis of organic chemistry, as for any other science, are its theoretical concepts. Russian chemists have always paid special attention to the fundamental rules. It is sufficient to name A. M. Butlerov, who created the structural theory, V. V. Markovnikov, well-known for the principal investigations into problems of the mutual interaction of atoms in a molecule, N. N. Menshutkin former pioneer of the use of kinetic methods of investigation in organic chemistry. This tradition lives on today.

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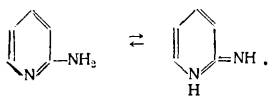
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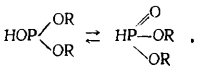
in the fields of physical chemistry, the chemistry of polymers, and chemical physics have significantly enriched organic chemistry both as regards understanding the significance of chemical changes and also from the methodological point of view. An examination of this question goes beyond the bounds of the present review; however, in this connection mention must be made of the development of the kinetics and theory of chain processes in the studies of N. N. Semenov and his school, the works of V. A. Kargin, V. V. Korshak, S. S. Medvedev, B. A. Dolgoplosk, N. S. Enikolopyan, G. L. Slonimskii in the field of polymer chemistry; the work of V. V. Voevodskii and P. A. Blyumenfel'd on the use of the EPR method; the quantum-mechanical studies of Ya. K. Syrkin, M. E. Dyatkina and others; work on X-ray structural analysis by A. I. Kitaigorodskii and others; M. G. Gonikberg and B. S. El'yanov's studies of reactions at high and superhigh pressures; the electrochemical work of A. N. Frumkin and his school; studies in the field of photochemical processes made by A. N. Terenin; and those of S. G. Mairanovskii in the field of polarography.

A. N. Bakh's work on oxidation in biological systems, the biochemical studies of I. E. Severin, A. N. Belozerskii, and A. S. Spirin, and the work of M. M. Dubinin and I. A. Rappoport on chemical mutagens are of great importance.

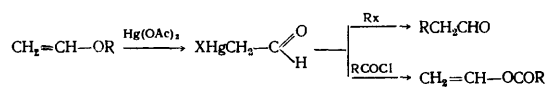
Soviet organic chemistry has great fundamental achievements in various fields of theoretical organic chemistry connected with the study of tautomerism and dual reactivity, the mechanisms of organic reactions, skeleton rearrangements, stereochemistry, etc. As is well known, the phenomenon of tautomerism—equilibrium isomerism—was first considered by A. M. Butlerov. The work on the problem of tautomerism and the closely connected problems of dual reactivity began more than a century ago and is still continuing. Soviet chemists have paid great attention to this problem. Thus Chichibabin discovered the tautomerism of 2-aminopyridine [1]:



A. E. Arbuzov studied an interesting new form of tautomerism by the example of dialkyl phosphites [2,3]:



The work of A. N. Nesmeyanov and M. I. Kabachnik is of special importance in this field. Nesmeyanov's school made extensive studies of the dual reactivity of organometallic compounds in the absence of tautomerism. Thus Nesmeyanov, Freidlina, and Borisov obtained many unsaturated compounds of mercury, gallium, lead, and antimony, capable of a dual reaction and named "quasicomplex" compounds by virtue of the easy elimination of the unsaturated compound under the action of complexing agents [4,5]. Nesmeyanov and Lutsenko found a very clear instance of dual reactivity of non-tautomeric substances in the compound β-chloromercuriacetaldehyde [7-9]:



Subsequently Nesmeyanov and Sazonova studied the geometrical isomers of (β,β-diphenylpropionyl)mesitylene enolates, which enabled them to draw conclusions about the absence of a tautomeric equilibrium between the metal enolates and the keto-form and the C-alkyl forms which were obtained on carrying out the reaction with "transfer of the reaction centre" [10-12]. In this series of investigations the regions of tautomerism and dual reactivity were first demarcated; it was shown that the latter is wider than the former: dual reactivity is a more general property of compounds with conjugated bonds. In these investigations the conjugation of triple bonds was extensively examined. Subsequently Nesmeyanov and Kabachnik surveyed the experimental results on the problem of the relation between dual reactivity and tautomerism [13]. It was shown that it is possible for two series of derivatives to be formed from a single form; here dual reactivity is the consequence of the special electronic structure of the conjugated system (for example, πσ-conjugation). The reactions of πσ-conjugated systems are now being broadly studied by I. F. Lutsenko (see p. 835). It is interesting to note that the fragmentation decomposition in the reactions of carbonium ions which has been widely studied by Grob's school [14] is evidently a further development of the ideas about πσ-conjugation [15]. The problems of dual reactivity were recently studied by Novikov and Tartakovskii by the example of trinitromethane derivatives [16]. A new approach to the problem of dual reactivity of the enolates of acetoacetic ester is being developed by Reutov, Beletskaya, and Kurts with the use of the concept of "nucleophilic cooperation" in reactions of organometallic compounds (see p. 819). [17]

The greatest achievement in the field of tautomerism proper is connected with the work of M. I. Kabachnik and his school. By applying the Brønsted equation to prototropic tautomeric equilibria, Kabachnik developed a quantitative theory of tautomerism [18,19]: he derived fundamental relationships which were governed by the position of the tautomeric equilibrium as a function of acidity:

$$K_T = \frac{k_{a_I}}{k_{a_{II}}} \frac{f_I}{f_{II}}$$

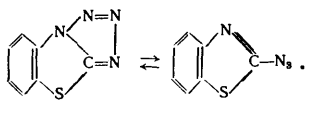
and which reflect the effect of the medium on the position of the equilibrium:

$$pK_{TS_I} = pK_{TS_{II}} + \text{const}\ .$$

These two fundamental equations enabled an explanation to be found for such dependences as the relation of acidity to enolisability, and gave a theoretical explanation for empirical relations found earlier, for example, the formulae of Meyer and Dimrot [18-21]. Kabachnik, with his students Ioffe, Mastryukova, Polikarpov, and Gilyarov, made a detailed investigation of the problems of the tautomerism of keto–enols, lactim–lactams, organophosphorus thion–thiols, diaryl- and amidodialkyl-phosphites, and phosphamidines [22-26]. By using the quantitative relationships found by M. I. Kabachnik, Sheinker studied the tautomerism of various heterocyclic compounds, such as acylaminopyridines, aminothiazoles, etc. [27,28]

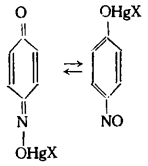
The use of correlation ratios enabled Kabachnik and Mastryukova to explain the departure from a simple linear relationship of the Hammett type for tautomeric systems and to derive a new equation with the aid of which equilibrium constants could be calculated [29].

Of the other studies in the field of tautomeric changes mention must be made of Postovskii's study of tetrazole–azide tautomerism [30]:



We note also the work of Novikov, Fainzil'berg, and Tartakovskii on acid equilibrium for polynitroalkanes, where the absence of the formation of an aci-form was demonstrated[31].

Of great fundamental interest is metallotropy, which was discovered and studied by Nesmeyanov and Kravtsov by the example of mercurated nitrosophenols[32,33]:



The study of the mechanisms of organic reactions is one of the key questions of organic chemistry; almost every organic chemist encounters these problems to some extent. The many investigations cannot be listed here and we will discuss the work of the main theoretical schools.

The most diverse problems of physical organic chemistry and the reaction mechanisms were studied in the work of O. A. Reutov, O. P. Beletskaya, and their students. Their main research deals with the mechanisms of electrophilic substitutions, by the example of organomercury compounds. Combined investigation of the stereochemistry (begun together with A. N. Nesmeyanov)[34] and kinetics of substitution of saturated organomercury compounds allowed a rule to be formulated about the retention of configuration in reactions which proceed by an S_E2 mechanism[34-39]. This rule can now be used to find the configuration of various functional derivatives of mercury[40,41].

The kinetic study of electrophilic substitutions of organomercury compounds of the aliphatic, aromatic, and alkenic series allowed general rules to be found for electrophilic substitutions at carbon atoms in various states of hybridisation. It was shown that a change in the structure or medium leads to a change in the bimolecular mechanism of the reaction to a unimolecular type S_E1.[37,42-44] A type S_E1 mechanism could be realised for all the types of carbon atom studied. It is especially interesting that the configuration at an alkenic carbon atom is retained, in accordance with the Nesmeyanov–Borisov rule, which will be discussed below, not only in S_E2 reactions, but also in reactions which take place by an S_E1 mechanism.

As a result of a study of much experimental material, the concepts of "inner" and "outer" nucleophilic catalysis have been created and it has been shown that catalysis of the latter type plays the decisive part in the realisation of electrophilic substitutions in several asymmetric organomercury compounds. This concept evidently has general significance in the reaction of organometallic compounds[33]. We note here that similar ideas about the role of complex formation for reactions of organoelemental compounds are being developed by Okhlobystin[45].

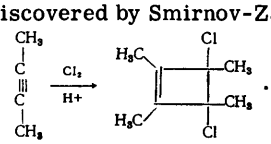
O. A. Reutov, I. P. Beletskaya, and K. P. Butin investigated the mechanisms of polarographic reduction of various types of organomercury compounds and showed the possibility of correlating the parameters of the electrolytic reduction $\alpha E_{1/2}$ of the symmetrical organomercury compounds R_2Hg with the pK_α of the corresponding hydrocarbons R–H. On the basis of the correlation obtained, a most complete scale of the acidity of hydrocarbons was compiled[46]. In this connection note must be taken of the systematic studies of the polarography of organic compounds made by Mairanovskii[47] and Stradin'[48].

Shatenshtein and coworkers undertook a very extensive investigation to find the acidities of hydrocarbons with the aid of a study of reactions of isotopic exchange in the ammonia–potassium amide system[49,50]. In these papers the view was first expressed that isotopic exchange reactions and metallation reactions belong to a general type of protophilic reactions in which the limiting stage is the loss of a proton and the formation of a carbanion. With the works of Shatenshtein a systematic investigation began into the influence of the solvent and the structural factors in various anionic reactions (isotopic exchange, metallation, Wurtz reaction, the formation of anion-radicals) and the exceptional role of specific solvation in all the processes studied has been demonstrated.

It is difficult to overestimate the value of isotopic methods to study the mechanisms of the reactions. The founders of this method in the USSR were A. I. Brodskii, G. P. Miklukhin, and A. I. Shatenshtein. We will also mention the systematic investigations on deuterio-exchange in hydrocarbons carried out by Kursanov, Setkina, and Parnes[51,52]. Many of the studies of these investigators were devoted to an investigation of hydride transformations. Mention must also be made of the work of Gragerov on the mechanisms of reactions by an isotopic method[53,54].

Under the direction of B. A. Arbuzov an extensive research was mounted to study organic compounds by physicochemical methods. Thus with the aid of parachor measurements B. A. Arbuzov succeeded in showing a series of details of the structure of esters of phosphoric, orthocarbonic, orthosilicic, formic, and phosphinic acids, and in studying the nature of the intermolecular interaction. Some interesting studies of reactions were made by the thermographic method. Together with Vereshchagin, systematic investigations were made into the configuration of addition products of diene synthesis by the dipole moments method[55]. Finally, B. A. Arbuzov and Yu. Yu. Samitov were the pioneers in the USSR in the use of the NMR method[56,57] in organic chemistry. Many series of papers by these authors deal with the study of conformations of α-oxides of the terpene series, 1,3-dioxanes, cyclic sulphites, etc.

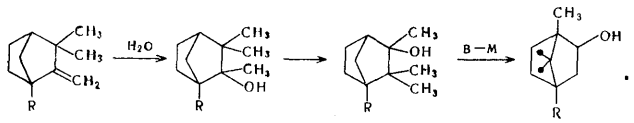
A systematic kinetic study of additions to alkenes was undertaken by E. A. Shilov and his student Smirnov-Zamkov. The study of these processes allowed Shilov to formulate the general principle of reactions proceeding through cyclic transition states[58,59]. The important role of termolecular complexes in heterolytic reactions was clearly demonstrated for the first time in the works of this school. The dimerisation of alkynes during chlorination is a very interesting reaction discovered by Smirnov-Zamkov[60]:



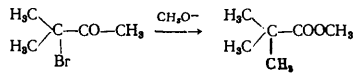
Such non-thermal reactions for cycloaddition are of great synthetic and theoretical interest.

Correlation equations are now widely used for solving many theoretical problems connected with reaction mechanisms. Pal'm[61] gave a theoretical basis for the principle of the linearities of free energies which lies at the basis of these equations. The correlation equations thus obtained were widely used for solving detailed problems of electronic structure, reactivity, and transmission of electronic effects by A. N. Nesmeyanov, E. G. Perevalova, S. I. Gubkin, M. I. Kabachnik, T. A. Mastryukova and V. A. Gilyarov, L. M. Litvinenko, Yu. A. Zhdanov, and V. I. Minkin.

Chemists have always been interested in rearrangements. Russian scientists have made a large contribution to this field of organic chemistry, and it is sufficient to remember the "celebrated" rearrangements of Wagner, Arbuzov, and Dem'yanov. Nametkin and his students discovered a new skeletal rearrangement, which is named after this investigator [62]:



The rearrangement of halogeno-ketones discovered by Favorskii [63] and bearing his name [64] is of enormous synthetic value:

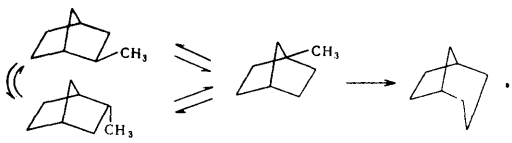


This rearrangement is widely used for the synthesis of various polycyclic and frame structures; it will be remembered that the synthesis of cubane includes a Favorskii rearrangement at two stages [65].

It is not accidental that Favorskii's students have paid great attention to studying skeleton rearrangements and related processes. The extensive investigations in the field of molecular rearrangements made by Danilov, Venus-Danilov [66], and Temnikova [67] are well known.

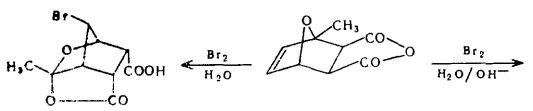
In recent years great attention has been paid to detailed aspects of the mechanisms of skeleton rearrangements. Thus Reutov and Shatkina have shown that in the deamination of propylamine a skeleton rearrangement does not take place; the observable distribution of an isotope tracer shows only the occurrence of a 1,3-hydride displacement [68]. Subsequently Reutov and Bundel' made a detailed study of carbonium ion rearrangements [69,70].

Plate, Belikova, and Mil'vitskaya [71-73] investigated the rearrangement of bicyclic hydrocarbons under the influence of acid, alkaline, and metallic catalysts. As an example we give the isomerisation of 2-methylnorbornane, which proceeds by the scheme:

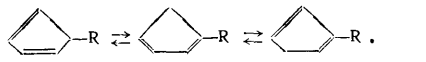


In a similar way the rearrangement of bicyclic hydrocarbons with eight and ten carbon atoms was studied in a similar manner [74].

Yur'ev and Zefirov studied several problems connected with the factors which determine the skeleton rearrangement in additions at a double bond and during the opening of α-oxides [75,76]:



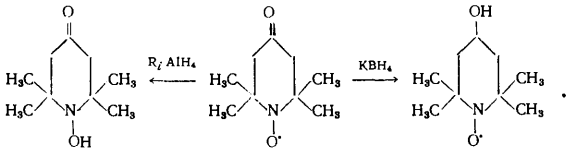
V. A. Mironov and A. N. Elizarova made interesting investigations in the field which is now unified under the name "valency tautomerisation and isomerisation". They studied the migration of double bonds in cyclopentadiene and its various homologues and showed that at low temperatures (depending on the type and extent of substitution) substituted cyclopentadienes—including deuteriocyclopentadiene—can exist as one of the isomers with a fixed position of the double bonds. On raising the temperature the double bonds migrate, and for substituted cyclopentadienes this leads to structural isomers:



Such isomerisation takes place in stages, and in several instances separate structural isomers can be isolated. It is interesting that the diene synthesis of cyclopentadienes with maleic anhydride can proceed without isomerisation of the double bonds [77,78].

Mention must be made of the theoretical studies of N. N. Vorozhtsov, Jnr. and V. A. Koptyug on rearrangements in aromatic systems. Extensive use of physical methods and particularly labelled atoms and NMR made possible a detailed investigation of various rearrangements in aromatic systems connected with the migration of a proton, or alkyl groups, and the explanation of the part played by acid catalysts. The extensive use of kinetic methods enabled several results of prime importance to be obtained on the mechanisms of the nucleophilic replacement of halogen, sulpho-, and nitro-groups. Of special interest is the study of the migration of methyl groups in polymethylbenzenonium ions [79,80].

The important role of free radicals in the most diverse chemical processes is now widely known. Note that in the field of the chemistry of stable free radicals a great part was played by the work of A. E. Chichibabin of the pre-revolutionary period. Work on the synthesis and study of the properties of stable radicals has continued ever since; in this connection note can be taken of Neiman and Rozantsev's work on the chemistry of iminoxyl free radicals [81]. These authors were the first to show the possibility of effecting the chemical conversions of these compounds without utilisation of the unshared electron:



Unstable free radicals were studied long ago by the school of N. N. Semenov. Thanks to these investigations the kinetics of chain gas reactions have been investigated in much greater detail than any other class of organic reactions.

The investigation of liquid-phase radical reactions began in the USSR with the works of Razuvaev and Koton by the example of the thermal decomposition of organomercury compounds [82]. Subsequently G. A. Razuvaev systematically studied the most diverse problems connected with the chemistry of free radicals in solution. As sources of free radicals, the photolysis and thermolysis of organic derivatives of lithium, zinc, mercury, aluminium, titanium, silicon, tin, and lead were studied [83-85]. Problems connected with the mechanism of the oxidation of organic derivatives of magnesium, zinc, cadmium, boron, aluminium, and mercury were investigated.

A long series of papers by R. Kh. Freidlina and coworkers was devoted to the study of the rearrangement of radicals in solutions. Until these appeared the very possibility of

skeleton isomerisations of radicals in solution was doubted. The investigations of Nesmeyanov and Freidlina showed that the CCl_3 group is active in reactions of a homolytic nature[86]. In a detailed study of the chlorination of hydrocarbons many instances were found of homolytic rearrangements, for example:

$$CCl_3CBr{=}CH_2 \rightarrow CCl_2{=}CCl{-}CH_2Br\ .$$

Subsequently the general character of homolytic rearrangements was discovered[87]. It is interesting that homolytic rearrangements with the 1,2-migration of chlorine were observed in the polymerisation of trichloroethylene[88].

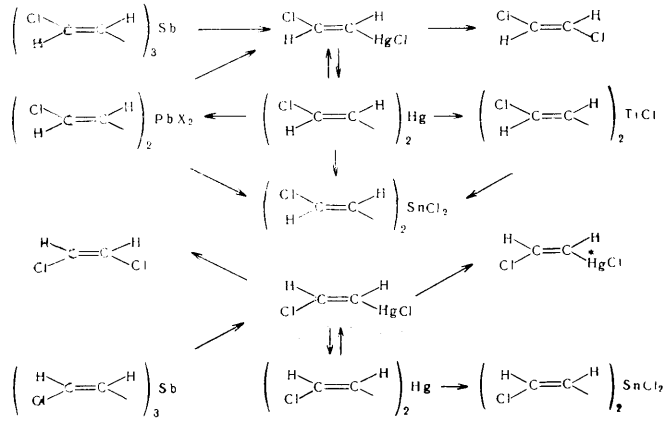
In addition, Reutov and Shatkina found that the propyl radical formed in the thermal decomposition of butyryl peroxide labelled in the α position undergoes rearrangement (to 4% extent), with 1,3-migration of hydrogen[89]:

$$CH_3CH_2\overset{14}{C}H_2\cdot \rightarrow \cdot CH_2CH_2\overset{14}{C}H_3\ .$$

Stereochemical studies carried out in the Soviet Union deal with the most varied aspects of this subject. Here the work of A. P. Terent'ev and his students must be mentioned first of all. Thus Terent'ev and Klabunovskii showed the possibility in principle of carrying out an asymmetric catalytic synthesis on the laevo- and dextro-crystalline modifications of quartz[90,91]. In the studies of Terent'ev and Potapov the spectropolarimetric method was used for the first time in the USSR to investigate the most varied compounds (nitrogen-containing heterocycles, Schiff bases, etc.)[92-95]. In investigating the rotatory dispersion (RD) of Schiff bases these authors observed a complex relation between the form of the RD curves and the solvent. This relation was used to explain detailed features of the structure of a series of compounds distinguished by solvation, etc. Spectropolarimetry was successfully used in association with reduction methods for the analysis of perfumery and food products.

Reference must also be made to the work of Kamai and Klabunovskii on the separation of arsenic derivatives by adsorption on quartz[96,97]; Levchenko and Kozlov separated derivatives of tetra-substituted sulphur into antipodes[98].

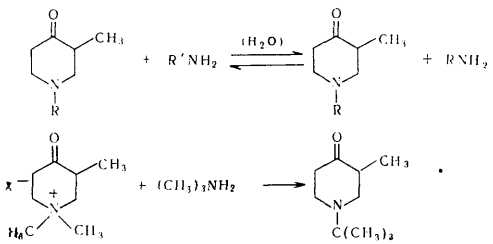
The stereochemistry of electrophilic substitution was examined in detail by A. N. Nesmeyanov. From extensive experimental material Nesmayanov and Borisov showed that homolytic and electrophilic substitutions at an alkene carbon atom proceed with retention of the configuration[99-104]:



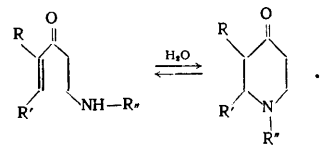
The stereochemical studies of O. A. Reutov in the field of electrophilic substitutions have been mentioned above.

Nazarov, Kucherov, and their students made a series of investigations into the steric and structural directionality of the reactions of the diene synthesis[105]. Subsequently V. F. Kucherov, N. Ya. Grigor'ev, V. M. Andreev, E. P. Serebryakov, and A. S. Onishchenko extensively studied the influence of conformational factors on the conjugation of unsaturated groupings in cyclic systems, on the direction of the initial attack in additions at a multiple bond in mono-, di-, and tri-cyclic systems, and studied the stereochemistry of epoxidation and bromination of derivatives of norbornene, cyclohexene, unsaturated derivatives of decalin, hydrindane, etc.[106-108]

Kucherov and Mistryukov investigated the influence of conformational equilibrium on the reactivity of piperidine derivatives[109-111]. They found an "amino-exchange" in piperidines which is unique in the ease of reaction[111]:

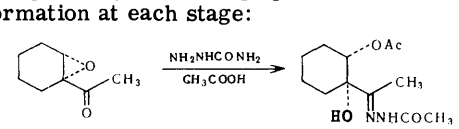


Mistryukov made a detailed investigation of the reversible cyclisation of $\alpha\beta$-unsaturated amino-ketones as a function of the substituent[112]:



The studies of V. F. Kucherov, A. V. Semenovskii, and V. A. Smit on the acid cyclisation of isoprenoids is of special interest. They succeeded in selecting experimental conditions (nitroalkanes, 100% sulphuric acid) such that the cyclisation takes place with high yield and is structurally unambiguous. By selecting catalysts which initiate cyclisation the authors could ensure a completely stereospecific process at all centres and hence model the process of the biological cyclisation of terpenoids[113].

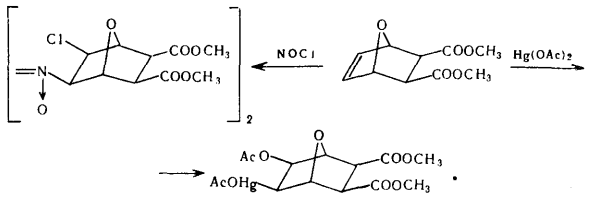
The stereochemical studies of A. A. Akhrem and his coworkers mainly developed in two directions. On the one hand there was the stereochemistry of nucleophilic addition at a carbonyl group. Akhrem and Kamernitskii examined much experimental material for the influence on the stereochemistry of nucleophilic addition of such factors as the conformation of the initial molecule, the dipole–dipole interaction of the functional groups and attacking agent, etc.[114,115]. The second direction is connected with a study of the interesting reaction of cis-opening of an α-oxide ring in keto-oxides under the action of various nucleophilic agents. Study of the mechanism of this reaction showed that this is probably a two-stage process with reversal of the conformation at each stage:



This reaction is used in steroid chemistry[116,117].

Yur'ev and Zefirov[118,119] studied the stereochemistry of the addition of electrophilic agents at a double bond in the 7-oxabicyclo[2,2,1]heptene system. They found an instance

of the cis-addition of weak electrophilic agents to the double bond:



A survey of the information on stereochemistry and the direction of electrophilic addition allowed these authors to advance the general concept of the dependence of the products of addition on alkene type, the electrophilic nature of the attacking agent, the nucleophilic nature of the anion, the polarity of the solvent, and additional stabilisation of the intermediate carbonium ion form of the substituent [119-121].

The studies of M. M. Shemyakin and L. D. Bergel'son showed that the stereochemical course of a Wittig reaction depends on the experimental conditions. The authors developed a variant of this reaction which leads almost exclusively to *cis*-alkenes. Subsequently this reaction was widely used for the synthesis of various natural unsaturated fatty acids [122], for example:

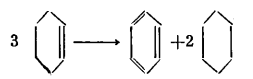
$$CH_3[CH_2]_nCHO + (C_6H_5)_3P{=}CH[CH_2]_7COOCH_3 \rightarrow CH_3[CH_2]_n{-}CH{=}CH{-}[CH_2]_7COOCH_3$$

The foundation for the chemistry of hydrocarbons was laid in our country by the investigations of the school of N. D. Zelinskii and A. E. Favorskii. Zelinskii's work in this field was extremely varied. Use of a combination of chemical and physicochemical methods allowed N. D. Zelinskii, S. S. Nametkin, N. I. Shuikin, and Yu. K. Yur'ev to study the composition of petroleums from all the main oil-bearing regions of our country. Inter alia they improved the old methods of refining and processing petroleum and developed methods new in principle, which allowed it to be converted into a promising starting material for the synthesis of various functional derivatives. The whole variety of these compounds was united by Zelinskii by the expression "products of the highest chemical value obtainable from petroleum hydrocarbons".

Kazanskii and Plate [123,124] discovered the reaction for C_6-dehydrocyclisation of alkanes in the presence of Pt/C. Similar reactions were effected simultaneously at higher temperatures by Moldavskii and Kamusher [125] on Cr_2O_3 and by Karzhev [126] on Cr–Cu phosphate catalyst. These reactions and their mechanism were thoroughly studied by Kazanskii and Zelinskii with the participation of Plate, Liberman, Sergienko, Rozengart, and others [127]. Active catalysts were found [128] which enabled benzene to be made industrially from petroleum hexane [129]. Kazanskii and Liberman discovered and studied in detail the C_5-dehydrocyclisation of alkanes into cyclopentanes [130]. Khromov together with these authors [131] found that 8-, 9-, and 10-membered rings are capable of transannular C_5- and C_6-dehydrocyclisation.

A new reaction for the hydrogenolysis of a 5-membered ring was effected by Kazanskii, Plate, and Zelinskii [132] and subsequently studied in detail [133].

Zelinskii discovered, and together with Pavlov, Kazanskii, and Levina [134] investigated, the reaction of "irreversible catalysis"—the redistribution of hydrogen in partly hydrogenated six-membered rings, with the simultaneous formation of more saturated six-membered and benzene rings. Gryaznov [135] studied the mechanism of these processes:



A reaction discovered by Zelinskii as long ago as 1911, the dehydrogenation of cyclohexanes, individually and in petroleum fractions, on Pt, Pd, and Ni/Al_2O_3 catalysts, found by him then for vapour-phase hydrogenation, has been thoroughly studied [134-138]. Yu. K. Yur'ev, P. P. Borisov, I. N. Tits-Skvortsova, N. I. Shuikin, R. Ya. Levina, A. F. Plate, A. M. Rubinshtein, Ya. I. Denisenko, and G. D. Gal'pern participated in these investigations. This is one of the reactions which lie at the basis of the well-known process of "platforming".

By studying the kinetics and mechanism of dehydrogenation of cyclohexanes, Balandin created the multiplet theory of catalysis, making use initially of the principle of structural [139-141], and then also energetic, correspondence between the reagents and catalyst [140], which stimulated work on the determination of the energies of the bonds between the reacting atoms and catalysts (Tolstopyatova [142] and Kiperman [143]). It was shown that [144-147] that reactions on oxides proceed by a doublet scheme with edge orientation of the ring, unlike the reactions on platinum and palladium, which proceed by a sextet model with planar orientation of the ring.

There have been very extensive investigations of the dehydrogenation of alkanes and alkenes to dienes, alkylbenzenes, and styrenes and also cyclopentanes to cyclopentenes, and further to cyclopentadienes. Zelinskii, Balandin, Marushkin, Bogdanova, Shcheglova, Isagulyants, Kazanskii, Sterligov, Shuikin, Smirnov, Lavrovskii, Lyubarskii, Sergienko, Rapoport, and others participated in these studies [148-161].

Liquid-phase hydrogenation catalysis is widely represented in the research of Zelinskii [134] and his school (Kazanskii, Sokol'skii, Freidlin [162-167]). The investigations of Levina and Skvarchenko [168,169] and also Kazanskii and coworkers [170,171] on reduction by hydrogen at the "moment of liberation" touch on this work.

The isomerisation of cyclic hydrocarbons under the action of Lewis acids—$AlCl_3$ and $AlBr_3$—was investigated by Zelinskii and Turova-Polyak [172-175], and Plate [71,74] investigated that of bicyclic hydrocarbons. Topchiev, Paushkin, A. D. Petrov, Sergienko, A. A. Petrov, and others studied the isomeric transformations of aliphatic hydrocarbons [148,176-179]. The work begun in our country by Ipat'ev [180] on the conversion of hydrocarbons under pressure, was continued in particular by Shuikin, Novikov, Minachev, and others [181-185] with the use of new catalysts. Gonikberg [186] studied the reactions of hydrocarbons and their derivatives, especially those with steric hindrance, under very high pressures. The alkylation of hydrocarbons was widely investigated by Topchiev, Yu. G. Mamedaliev, G. M. Mamedaliev, Lavrovskii, Shuikin, Viktorova, Panchenkov, Paushkin, Tsukervanik, Freidlin, and others [187-197]. The work on the cracking and pyrolysis of hydrocarbons begun even before the revolution and developed during its first years by N. D. Zelinskii was continued by Byzov, Lebedev, Topchiev, Voevodskii, and also by Lavrovskii and Brodskii, Agafonov, Topchieva, Paushkin, Panchenkov, and others [198-210]. After the pioneering investigations of A. N. Bakh in the field of the oxidation of hydrocarbons, important contributions were made by N. N. Semenov, N. M. Emanuel', S. S. Medvedev,

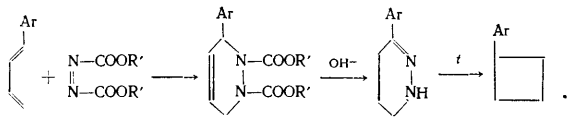
S. S. Nametkin, A. N. Bashkirov, and V. V. Kamzolkin, K. I. Ivanov, D. S. Velikovskii, K. K. Dubrovai, I. P. Losev, P. A. Moshkin, S. Z. Roginskii, and L. Ya. Margolis, P. V. Zimakov, V. Ya. Shtern, N. I. Chernozhukov, S. E. Krein, V. K. Tsyskovskii, and others[211-214].

In the field of polymerisation and condensation we will note the reaction of cross-dimerisation of acetylene into 2-methylpropene (Petrov[215]), and the dimerisation of ethylene (Eidus, Kazanskii and coworkers[216-223]).

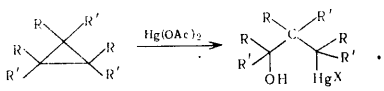
Physical and physicochemical investigations of catalysts for hydrocarbon conversions are represented in the works of Rubinshtein and coworkers[224,225] the rules for reactions in a monolayer in the studies of Vasserberg[226], and the stereochemical aspects of catalysis in those of Klabunovskii[227]. Klabunovskii's studies of the regularity of the configurational correlations in asymmetric catalysis are of great interest[227].

The work in the field of small rings is of great theoretical importance. N. M. Kizhner developed the celebrated method of synthesis of cyclopropanes through pyrazolines from $\alpha\beta$-unsaturated carbonyl compounds. In a long series of papers Levina and Shabarov studied the conjugation of a three-membered ring with a benzene ring[228].

Levina and Shabarov developed an original method for the synthesis of arylcyclobutanes on the basis of a diene synthesis with azodicarboxylic ester[228]:

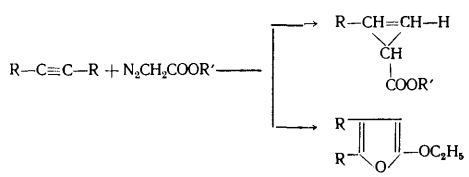


A study of the chemical and physical properties of derivatives of small rings enabled the specific characteristics of their electronic structure to be distinguished clearly. The especially marked relationship between cyclopropanes and alkenes was demonstrated by Levina in studying the opening of a three-membered ring by mercury salts[229]:



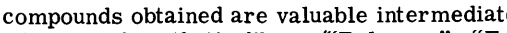
Here we can add the work of Kazanskii and Lukina on the study of the hydrogenolysis of small rings[229a].

Here mention must also be made of the work of D'yakonov and coworkers on the synthesis of derivatives of cyclopropane and cyclopropene on the basis of the reactions of diazo-compounds with alkenes[230]. The synthesis of cyclopropenes by the reaction of diazoacetic ester with acetylenes by the scheme[231]:

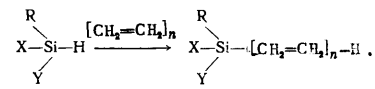


is especially interesting.

A. N. Nesmeyanov and R. Kh. Freidlina have shown that the telomerisation of alkenes with carbon tetrachloride and chloroform allows various $\alpha\alpha\alpha\omega$-tetrachloroalkanes to be obtained; these are intermediates in the synthesis of ω-amino-acids. Subsequently, R. Kh. Freidlina, L. I. Zakharkin, and V. N. Kost made a detailed investigation of the production of aminoheptanoic and aminononanoic acids according to the scheme:

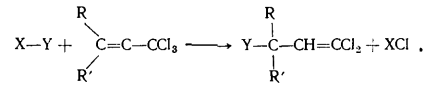


The compounds obtained are valuable intermediates in the manufacture of synthetic fibres ("Pelargon", "Enant"). Methods were also developed for the synthesis of α-amino-acids of the most varied structures and also thiols, sulphides, sulphenyl chlorides, and sulphonic acids. The compounds obtained are of undoubted interest as plasticisers, perfumes, lubricants, and intermediates for organic synthesis[232-237]. This reaction is especially interesting for the synthesis of organosilicon compounds. It was found that alkenes undergo telomerisation with silanes containing an Si–H bond, as follows[238]:



The peculiarity of this reaction is that it takes place in the absence of initiators at 300°C and a pressure of 100–500 atm (thermal telomerisation). It was found subsequently that the addition of silicon hydrides to alkenes is catalysed by various compounds such as metal carbonyls, zirconium and titanium tetrachlorides, etc.

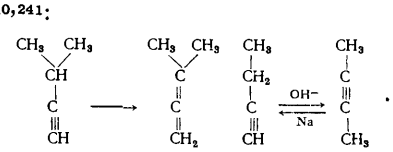
Of great significance in principle is an investigation, completed in connection with the study of telomerisation, into the chemical properties of compounds with the groupings CCl_3, CCl_3CHCl, $CCl_2{=}CH$, $CCl_3{=}C$, etc., and, in particular the action of various nucleophilic, electrophilic, and radical agents on these groupings. For example, it was shown that the action of nucleophilic agents on compounds with the $C{=}C{-}CCl_3$ grouping proceeds with rearrangement by the scheme[232]:



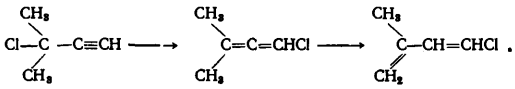
Finally, it is impossible to omit the extensive investigations of I. L. Knunyants in the field of polymer chemistry. In 1942–43, together with Rogovin and Rymashevskaya he first described the polymerisation of caprolactam into caprone. Later Knunyants proposed a new method of synthesis of adipodinitrile by the hydrodimerisation of acrylonitrile[239]. This method has great prospects in the production of nylon.

A very large group of papers by Soviet chemists is connected with the reactions of diene hydrocarbons, the greatest practical interest being in the investigations in the field of polymerisation, which started from the classical works of A. M. Butlerov. The development of this field of organic chemistry in the Soviet period is mainly associated with the name of Butlerov's student A. E. Favorskii, who created one of the largest chemical schools. His students included such celebrated chemists as Zh. I. Iotsich, S. V. Lebedev, I. N. Nazarov, M. F. Shostakovskii, V. A. Mokievskii, S. N. Danilov, T. A. Favorskaya, R. S. Zal'kind, B. V. Byzov, A. E. Porai-Koshits, and others.

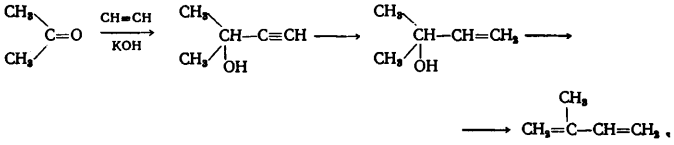
Even in the pre-Octobrian period Favorskii discovered the celebrated rearrangements of unsaturated compounds: acetylene–allene and the prototropic rearrangements of acetylenes[240,241]:



T. A. Favorskaya made thorough investigations of the acetylene–allene and allene–diene rearrangements of acetylenic halides, leading to chloroprene[242]:

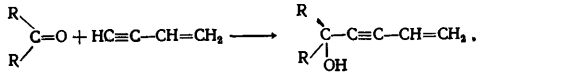


A. E. Favorskii discovered the reaction of alkaline condensation of acetylene with ketones, which made the alcohols of the acetylenic series readily accessible. A method of synthesising isoprene was developed on the basis of this reaction:

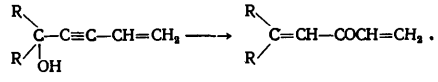


Subsequently this reaction was extensively used in the works of I. N. Nazarov and his students (V. F. Kucherov, L. D. Bergel'son, I. V. Torgov, A. A. Akhrem, I. L. Kotlyarevskii, and S. A. Vartanyan).

By using vinylacetylene as the acetylenic component in the Favorskii reaction, I. N. Nazarov succeeded in obtaining extremely reactive vinylethynylcarbinols:

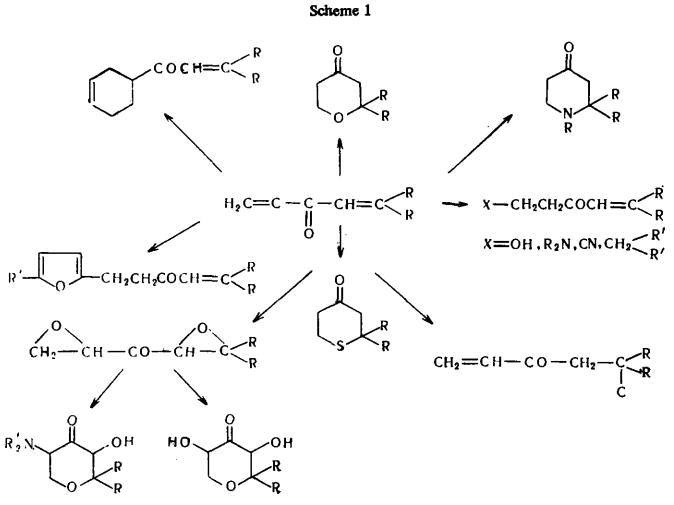


These compounds found practical application for the preparation of the so-called "carbinol glue". Vinylethynylcarbinols readily isomerise under the action of mercury salts into divinyl ketones:



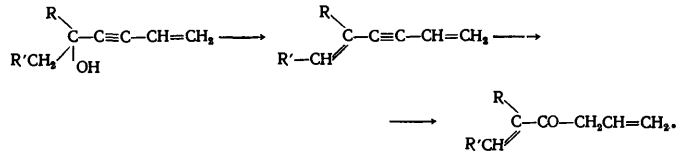
The latter were used for the synthesis of the most varied compounds[242–245], including those of the heterocyclic series, as Scheme 1 shows.

Scheme 1

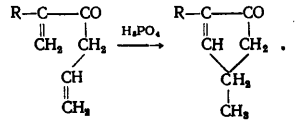


These studies of Nazarov and coworkers are well known and have been reviewed on several occasions[243]. Among the compounds obtained on the basis of the divinyl ketones are valuable pharmaceutical preparations—Promedol and Isopromedol[245].

The dehydration of vinylethynylcarbinols, leading to divinylacetylenic hydrocarbons, and the subsequent hydration of the latter leads to allyl vinyl ketones, which are very reactive compounds[243,246]:



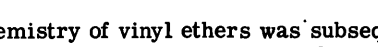
The cyclisation of allyl vinyl ketones under the action of acids leads to cyclopentenones:



Further development of this work consisted in the use of cyclopentenones in a diene synthesis to obtain polycyclic structures related to the steroids. These investigations served as the start of chemical research in the field of the synthesis and modification of steroids, which is developing successfully at the present time (A. A. Akhrem, I. V. Torgov, and S. N. Ananchenko).

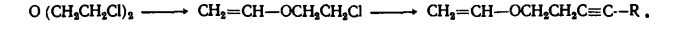
Mention must also be made of the work of Nazarov[247], Yanovskaya[248], and Mikhailov and Povarov[249–251] on the study of the condensation of acetals with vinyl esters which allowed various poly-unsaturated compounds similar in structure to the carotenoids to be obtained.

Favorskii and Shostakovskii developed a new method for the synthesis of vinyl ethers involving the reaction of acetylene with alcohols in the presence of alkali[252]:

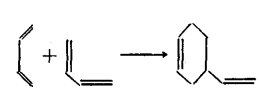


The chemistry of vinyl ethers was subsequently studied extensively by M. F. Shostakovskii. The hydrolysis, addition, and polymerisation of vinyl ethers was studied and a series of compounds was obtained which could be used as pharmaceutical preparations and solvents[253]. Shostakovskii and Prilezhaeva studied vinyl sulphides[254].

The work of Shostakovskii and Vlasov[255,256] on the production of polyfunctional vinyl ethers is especially interesting, for example[255]:

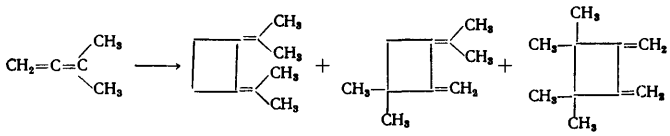


Another direction in the chemistry of diene hydrocarbons is associated with the name of S. V. Lebedev. Even in the pre-Octobrian period he began to study polymerisation processes; he investigated the polymerisation of 16 derivatives of divinyl. During this he formulated, long before the work of Diels and Alder, the principle of the condensation of diene hydrocarbons according to the scheme of the diene synthesis[257]:



We also note that cycloaddition leading to cyclobutanes[258] —a reaction now being widely studied—was also investi-

gated by Lebedev by the example of the dimerisation of allenes[257]:



Without exaggeration it can be said that until recently Lebedev's results on allene chemistry remained the main information in this field.

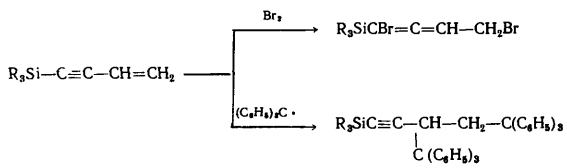
However, S. V. Lebedev's greatest contribution is connected with the creation of the synthetic rubber industry in the USSR. Lebedev and his students developed a single-stage catalytic method for the synthesis of divinyl from alcohol; simultaneously a method was developed for polymerisation by use of metallic sodium. The synthetic rubber industry created by the Soviet state on the basis of Lebedev's work has now attained great success and completely satisfies the requirements of the country's national economy.

The Lebedev process has now been considerably improved as a result of the work of his students, among whom were A. I. Yakubchik, D. M. Slobodina, M. D. Gordina, S. A. Subbotina, Yu. A. Gorina, and I. A. Volzhinskii.

Various types of polymerisation of unsaturated compounds are now widely studied in various centres of the USSR and their consideration goes beyond the bounds of the present review. We will note only the work of Dolgoplosk on stereospecific polymerisation[259,260], that of Klebanskii on chloroprene rubber[261], that of Shilov and coworkers on the mechanism of polymerisation on Ziegler catalysts[262], and also the studies of the coworkers of the Yaroslavl' Scientific Research Institute for Monomers, Fel'dblyum and Obeshchalova[263].

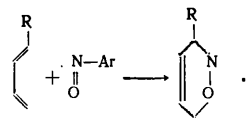
Many papers have been devoted to the study of the chemical properties in connection with the practical use of unsaturated hydrocarbons and in particular additions, the diene synthesis, 1,3-dipolar cycloaddition, etc.

First of all here we must note the extensive series of papers by A. A. Petrov who studied the addition of a wide variety of reagents, to diene, enyne, and diyne hydrocarbons[264-267]. The enyne derivatives of silicon are of especial interest; for them it was shown that the decisive factor which determines the direction of addition is $p_\pi d_\pi$-conjugation of the silicon atom and the double bond:

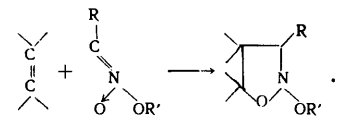


A. A. Petrov studied many acetylene derivatives of tin, phosphorus, and boron; they developed new methods of obtaining organophosphorus heterocycles based on the condensation of phosphides with dienes and $\alpha\beta$-unsaturated carbonyl compounds. As a result of studying the ionic telomerisation of unsaturated compounds with halogen derivatives, he developed an industrial method for the synthesis of citral from isoprene.

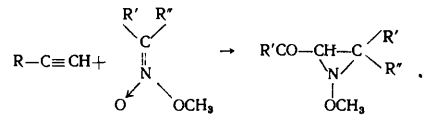
We note also here the work of Kazanskii and Levina on the hydrogenation of diene systems[268], that of Nazarov and Titov on the diene synthesis[269], that of Babayan on the synthesis of nitrogenous compounds from 1,3-dichlorobutane[270], that of B. A. Arbuzov and Konovalov on finding the mechanism of the diene synthesis[271]. A. N. Nesmeyanov and Yu. A. Arbuzov showed that aromatic nitroso-compounds can be used as the dienophile in the diene synthesis[272]:



The original reaction of 1,3-dipolar addition was discovered by Novikov and Tartakovskii, who used esters of the *aci*-form of nitro-compounds as the "1,3-dipole" [16]:



This reaction has been extended to a wide circle of alkenes and dienes. The reaction of acetylenes with these 1,3-dipoles leads to the production of aziridines by the scheme:



Machinskaya and Barkhash extensively studied methods of obtaining and the use in synthesis of the enol acetates of carbonyl compounds[273].

There is also the work of Perekalin[274] and Novikov and coworkers in the field of unsaturated nitro-compounds[275].

The development of the chemistry of aromatic compounds has been continually associated with the aniline dye and phamaceutical chemical industries. In this field, more than in any other, the main forces were directed towards assimilating the experience of foreign chemistry. M. I. Kabachnik took part in interpretation of the structure and the organisation of production of the first cyanine dyes. Conspicuous parts in the development of aniline dye chemistry were played by N. N. Vorozhtsov, Snr., N. N. Vorozhtsov, Jnr., A. E. Porai-Koshits, A. I. Kiprianov, and I. I. Levkoev. Soviet scientists paid special attention to the prolems of the theory of the colour of dyes. In this connection there is work of Izmail'skii on mesomerism[276], which in many respects preceded later ideas of foreign scientists; the work of Ioffe in the field of rhodamine dyes[277]; and that of Levkoev and Vompe, where problems of the dependence of the colour of cyanine dyes on the basicity of the heterocyclic nuclei were examined[278,279]. The work of A. I. Kiprianov is of great importance for the creation of a theory of colour. Critical problems of his work on the relation of the structure and colour of a dye are: the investigation of the influence of steric hindrance, the presence of polar substituents, and the absence of symmetry in the structure of the molecule and also the solvatochroism which is connected with this question. The concept he introduced of the dependence of the colour of polymethylene dyes on the equivalence of bonds in the chromophore of a dye was confirmed by studies in the field of unsymmetrical cyanine dyes. For the latter Kiprianov introduced the "hypsochromic shift" rule according to which with increase in the difference in the basicity or polarity of the terminal units of a chromophore there is an increase in the displacement of the absorption maximum towards shorter wavelengths from the arithmetic mean of the two corresponding symmetrical

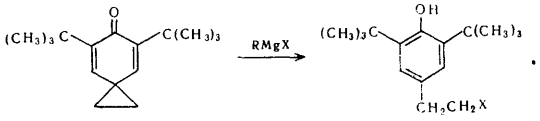
dyes[280]. Note also the work of A. I. Kiprianov on the synthesis of "Sanazine", a homologue of the natural antibiotic pyocyanine.

In addition to direct practical tasks Soviet chemists solved a series of questions of principle in the field of aromatic compounds. Here we must refer to the work of Vorozhtsov, Snr., and Bogdanov in the field of the chemistry of naphthalene derivatives[281,282], A. E. Porai-Koshits and B. A. Porai-Koshits on the structure and tautomerism of dyes, diazo-compounds, the mechanism of diazotisation, etc.[283], and that of Ioffe on the synthesis of binaphthyl derivatives[284].

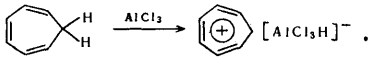
The work of Zeide and Dubinin on aromatic musks[285], and that of Rodionov on derivatives of opianic acid[286] belong to this field. Of the latter, there is special interest in the work of Belov and Kheifits on the alkylation of bicyclic terpenoids with phenols, which leads to the production of valuable perfumery preparations[287,288]. These reactions are interesting also from the theoretical standpoint, since the alkylation is accompanied by complex skeleton rearrangements and 2,6-hydride displacements.

Mention must also be made of the new method of synthesis of aromatic compounds developed by R. Ya. Levina and V. P. Skvarchenko. These authors found that addition products from the diene synthesis with maleic anhydride readily aromatise on heating with phosphorus(V) oxide; this method was used successfully to make homologues of benzene, naphthalene, anthracene, fluorene, and polynuclear aromatic hydrocarbons[289].

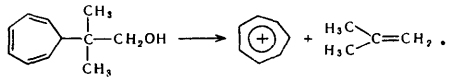
A long series of studies of the field of sterically hindered phenols was made by Ershov and Volod'kin[290,291]. By a large number of examples it was shown that *o,o*-di-t-butylphenol readily forms quinolide structures under the action of various electrophilic reagents. The authors have extensively investigated the dienone–phenol rearrangements that take place in this. The dienone–phenol rearrangement of spirane systems which they studied is especially interesting. For example, under the action of a Grignard reagent 4,6-di-t-butylspiro[2,5]octa-3,6-dien-5-one reacts with cleavage of a C–C bond to form derivatives of phenol by the scheme[290]:



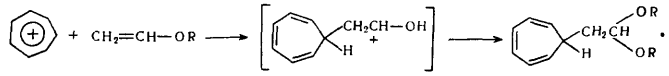
The problem of the structure of aromatic compounds and the reasons for their special properties is one of the central problems of theoretical organic chemistry. The development of quantum mechanics has significantly altered our views on the problem of aromaticity and has enabled a great number of compounds belonging to the class of non-benzenoid aromatic compounds (concerning π-complexes see below) to be obtained. The most important results in this field were obtained by D. N. Kursanov and M. E. Vol'pin. As they showed, under the action of the most varied electrophilic agents cycloheptatriene forms a tropylium salt by the scheme[291,292]:



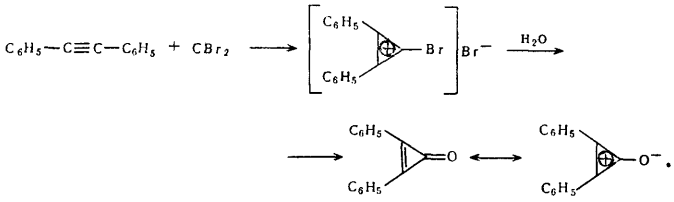
The formation of tropylium can take place even with fission of the C–C bond. For example, 2-cycloheptatrienyl-2,2-dimethylethanol decomposes extremely readily in the presence of acids with the formation of tropylium salts[294]:



As a result of the work of D. N. Kursanov and M. E. Vol'pin the "tropylation" reaction can be used as a means for determining reaction mechanisms. For examples, these authors studied the possibility of a carbonium ion being formed in the reactions of acetals, for which they carried out the reaction of the stable tropylium ion with ethyl vinyl ether, which confirmed the possibility of an acetal condensation by a carbonium ion scheme[295]:



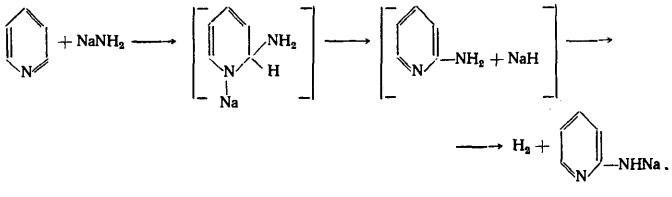
Another interesting direction of Kursanov and Vol'pin's work is connected with a three-membered aromatic system—diphenylcyclopropenone—which they succeeded in obtaining in the reaction of dichloro- and dibromo-carbene with tolane[296]:



As Syrkin and Shidlovskaya's investigation showed, diphenylcyclopropenone has a very high dipole moment, 5.08 D.[296] Of the other work on non-benzenoid aromatic compounds we will mention the investigations of Yashunskii and Kholodov on the chemistry of sydnones[297].

The chemistry of heterocyclic compounds is developing in our country at an explosive rate. Investigations in this field of organic chemistry enable new regularities in the behaviour of organic compounds to be discovered and facilitate the development of new theoretical concepts. On the other hand the enormous practical value of these investigations as a basis for creating new pharmacological preparations, dyes, plant growth regulators, and intermediates for fine organic synthesis is quite evident.

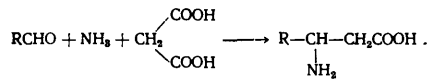
In this field it is necessary above all to refer to the investigations of A. E. Chichibabin. In 1914 Chichibabin and Zeide discovered the reaction of the amination of pyridine and its derivatives under the action of sodium amide, which has been given the name "Chichibabin reaction" in world literature[298–300]:



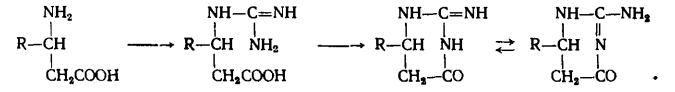
In the subsequent studies of Chichibabin and his school (O. A. Zeide, A. V. Kirsanov, I. L. Knunyants, N. N. Vorozhtsov, Z. V. Benevolenskaya, and A. F. Egorov) the chemistry of the amino-derivatives of pyridine, quinoline, pyrimidazole, and other heterocyclic systems was widely developed[299,300].

However, the chemistry of heterocyclic compounds underwent the greatest development in the post-war years; the chemists working in this field constitute one of the largest groups of Soviet organic chemists. The progress in this field is also shown by the appearance of the journal "Khimiya Geterotsiklicheskikh Soedinenii" [Chemistry of Heterocyclic Compounds] (published in Riga). Such great scientists as A. N. Nesmeyanov, V. M. Rodionov, I. L. Knunyants, Yu. K. Yur'ev, N. K. Kochetkov, amongst others, worked or are working in this field.

Rodionov developed a convenient method of synthesising β-amino-acids by the scheme [301,302]:

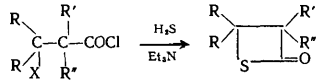


From β-amino-acids, V. M. Rodionov and coworkers synthesised various types of heterocyclic compound, such as glyoxalidones, pyrimidones, dihydrouracils, etc. As an example there is the synthesis of aminodihydropyrimidine [302]:



The first period of work of I. L. Knunyants was devoted to investigations in the field of the chemistry of nitrogen-containing heterocyclic compounds. He obtained various derivatives of alkylaminopyridines and also pyridine analogues of the dyes of the di- and tri-phenylmethane series. Mention must be made of the investigations in the field of cyanine dyes and also in that of acridine, on the basis of which the industrial production of Acrichin [atebrin] was organised.

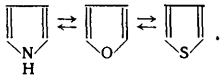
Knunyants and Lin'kova discovered a new class of four-membered heterocyclic system—β-propiothiolactone [303,304]. The most convenient method of synthesising derivatives of this class consists in the reaction of the acid chlorides of β-halogenocarbonyl compounds with hydrogen sulphide in the presence of triethylamine [303]:



Knunyants and coworkers effected a peptide synthesis based on β-thiolactones [305]. Knunyants and Kil'disheva studied the mutual relation of oxazolones and pseudo-oxazolones (2,4-disubstituted) and developed methods of establishing their structure [306].

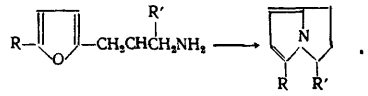
Together with Kil'disheva, Knunyants synthesised a large class of compounds containing a bis-β-chlorovinyl grouping and peptide chains which led to the creation of new mutagens, original cancerolytic preparations.

In 1935 Yur'ev discovered the reaction which bears his name, the interconversion of heterocycles under conditions of vapour-phase catalysis over aluminium oxide [307]:



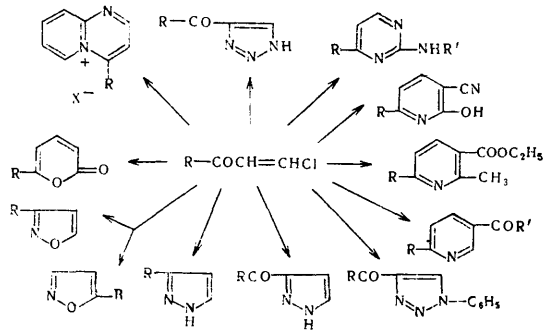
The conversion of the fully hydrogenated derivatives of these aromatic compounds takes place especially readily. In the extensive series of works of Yu. K. Yur'ev and coworkers (E. G. Vendel'shtein, I. K. Korobitsyn, and K. Yu. Novitskii) were synthesised a great number of varied heterocyclic systems [308].

A very interesting intramolecular variant is the Yur'ev reaction (Sorm, Ponomarev) which leads to a pyrrolizidine derivative [309,310]:

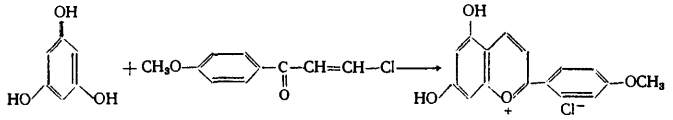


A general, unusually fruitful method of synthesis of a variety of heterocyclic compounds was developed by Nesmeyanov and Kochetkov on the basis of alkyl and aryl 2-chlorovinyl ketones—products of the condensation of acid chlorides with acetylene in the presence of aluminium chloride [311-313]. Scheme 2 shows the extensive theoretical possibilities of this method.

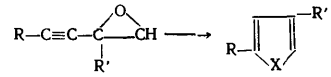
Scheme 2



Note that the reaction of β-chlorovinyl ketones with phenols takes place with the formation of benzopyrylium salts; in this way a natural anthocyanidin methyl ether, hesperidin, was synthesised from phloroglucinol and *p*-methoxyphenyl chlorovinyl ketone [314]:



Another general method of synthesis of various five-membered heterocyclic compounds was developed by Perveev and coworkers on the basis of acetylenic epoxides [315,316]

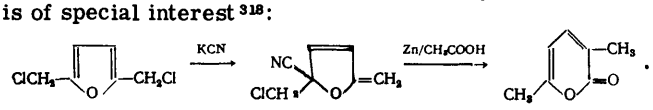


where X = NH, NR, S, O, Se.

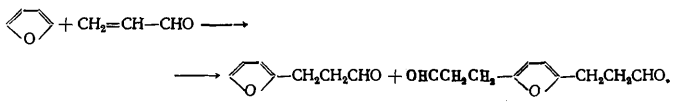
The general nature of this reaction was confirmed by the synthesis of many representatives of furan, thiophen, pyrrole, and selenophen.

Furan chemistry was extensively developed in the studies of Soviet investigators, this being directly connected with the problem of the use of pentosan-containing raw materials, the primary product of the treatment of which is furfural.

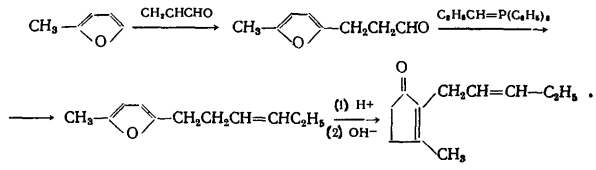
A great contribution was made in this region by Yu. K. Yur'ev and his school (K. Yu. Novitskii, N. K. Korobitsyna, N. S. Zefirov, V. P. Volkov, and M. A. Gal'bershtam). Yur'ev and Novitskii synthesised the most varied bifunctional derivatives of furan from bis(chloromethyl) derivatives of furan [317,318]. The example of an allyl rearrangement in the furan series which was found by these authors is of special interest [318]:



In 1938 Sherlin and Berlin and their coworkers showed that $\alpha\beta$-unsaturated carbonyl compounds react with furan by a substitutive addition[319]:



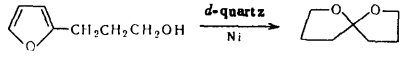
This reaction was subsequently studied by several authors[243]; however, only Yur'ev and Zefirov showed the general nature of this reaction[320]; it is now widely used for the synthesis of a variety of furan derivatives[321,322]. For an illustration we give the synthesis of jasmone, carried out by Yur'ev and Zefirov on the basis of this reaction[323]:



There is also the work of Yur'ev and Korobitsina on the synthesis of heterocycles from 3-keto- and 3,4-diketotetrahydrofurans[324], that of Yur'ev and Zefirov in the field of diene synthesis in the furan series[325], and that of Yur'ev and Gal'bershtam on the kinetics of the solvolysis of chloromethyl derivatives of heterocycles[326].

A great investigation on the synthesis, reactions, and practical applications of furan derivatives was carried out under the direction of S. A. Giller. Among the works of his school there are the development of a method of contact vapour-phase decarbonylation of furfural into furan (Karmil'chik[327]), the industrial synthesis of maleic anhydride from furfural (Shimanskaya[328]), work on the synthesis of physiologically active substances based on nitrofurans[329-331]; the alkylation of furan with alkenes (Berzin'[332]). The work of Stradin' and Giller on the polarography of the nitroderivatives of the furan series is especially interesting; it was shown that it was possible to study intermediate radicals by the EPR method[48,333].

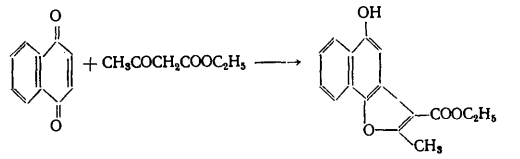
Ponomarev made extensive investigations in the field of furan chemistry[334]; the main directions were connected with a study of the catalytic hydrogenation of these compounds. We may note also Ponomarev and coworkers' study of the synthesis of optically active dioxaspirononanes from derivatives of tetrahydrofuran by the scheme[335]:



The hydrogenolysis of furan compounds was widely studied by N. I. Shuikin and his coworkers I. F. Bel'skii, R. A. Karakhanov, and V. M. Shostakovskii. They studied synthetically the catalytic hydrogenation of furan derivatives of the most diverse types, the isomerisation of γ- and δ-oxides, and the thermal and catalytic conversions of 2,5- and 2,3-dihydrofurans[336-338].

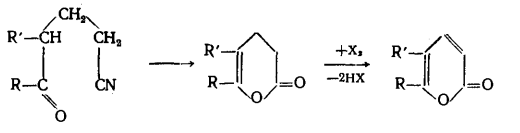
Mndzhoyan and coworkers[339-341] carried out systematic investigations to find physiologically active substances in the furan series. They tackled the problem of the chloromethylation of furan derivatives, on the basis of which they obtained an antitubercular preparation "Armazid" and a preparation against glaucoma "Dimefur". There are also papers by Nazarova[342], and Moshkin and Lutkova[343].

In the benzofuran field, mention must be made of the work of Terent'ev and Grinev, who developed a convenient method for the synthesis of the compounds of this series from p-quinones and acetoacetic ester[344]:



The compounds obtained were effective plant growth stimulators.

Levina and Shusherina developed a new method for the synthesis of 2-pyrones on the basis of δ-enol-lactones[345]:



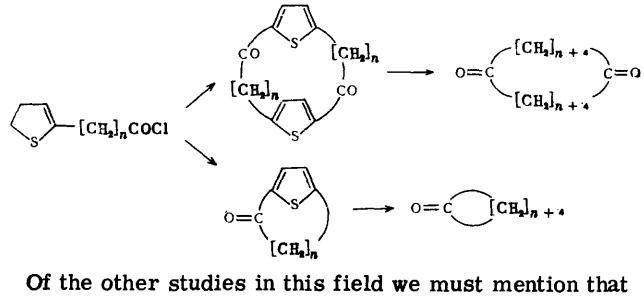
Subsequently these authors made detailed studies of electrophilic substitutions in the pyrone series and also investigated various conversions of the derivatives of this series. Zakharkin and Sorokina developed a new method for the synthesis of 2-pyrones based on the condensation of dichloroacrylaldehyde with compounds having a labile hydrogen atom (acetoacetic ester, pyrotartaric acid)[346]. Zhdanov and Dorofeenko synthesised pyrylium salts[347].

A new method for the sulphonation of acidophobic heterocyclic compounds was developed by Terent'ev and Kazitsina[348]. The sulphonation of furan, pyrrole, and their derivatives takes place smoothly under the action of pyridine–sulphur trioxide and leads to the mono- or the di-sulphonic acid, depending on the conditions.

Thiophen chemistry has formed the subject of broad systematic investigations by Ya. L. Gol'dfarb and his coworkers. The work on the synthesis of sulphides of the thiophen series has acquired an extensive scope; an effective method has been found for their synthesis from lithium derivatives of thiophen. A further development of these studies was the synthesis and study of conversions in the thiophen series[349].

Another type of reaction widely studied by Ya. L. Gol'dfarb, L. I. Belenkii, and coworkers is reduction desulphurisation. The removal of sulphur from thiophen derivatives by Raney nickel leads to aliphatic compounds. The use of this reaction enabled many difficultly accessible types of aliphatic and cyclic compounds to be obtained.

Among the compounds synthesised in this way are ketones from 14 to 17, 20, 26, and 28 carbon atoms in a ring; exaltone and dihydrocivetone were synthesised[349,350]. The following examples can serve as an illustration:



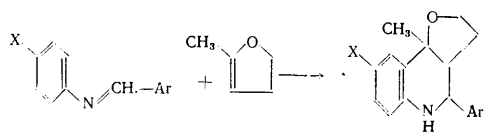
Of the other studies in this field we must mention that of Yur'ev, Elyakov, and Belyakova on the actylation of thiophen with silicoanhydrides[351,352], that of Tits-Skvortsova

and Danilova[353], and also Obolentsev on the destruction of thiophanes[354], and that of Yur'ev and Rozantsev on the synthesis of standard thiophanes[355].

The electrophilic substitutions and reactivity of selenophen derivatives and their synthesis have been extensively studied by Yur'ev, Magdesieva, and Sadova[356,357].

Some of the studies in the field of nitrogen-containing heterocycles were considered above. There are also the work of Putokhin on the application of Den'yanov's ring enlargement reaction to heterocycles[358], that of Chumakov on the synthesis of pyridines from 2-alkoxy-3,4-dihydropyranones[359], that of Kozlov on the synthesis of quinolines from aromatic amines and acetaldehyde[360], that of Pushkareva on the study of derivatives of quinaldine and acridine[361], that of Vanag on the synthesis of complex heterocyclic systems from β-dicarbonyl compounds[362,363], Rubtsov's synthesis of bicyclic compounds with a nitrogen atom at the head of the bridge[364], that of Yakhontov on azaindoles[365], Grigorovskii's study of the chemistry of the luminescent reactions of lucigenin[366], Prostakov's synthesis[367] of pyridine derivatives from piperidones, and Vompe's[368] synthesis of pyridine and quinoline derivatives.

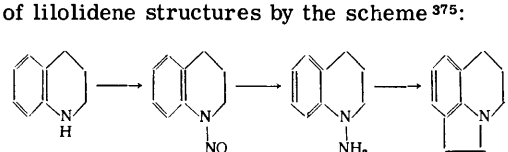
Povarov and Mikhailov developed a method of synthesising tetrahydroquinolines from alkyl vinyl ethers[241-251,369], for example:



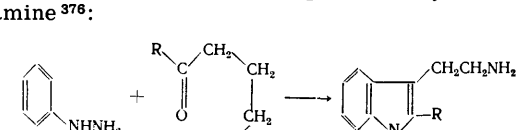
As is well known, indole derivatives play a large part in biochemical processes, therefore the great interest of Soviet chemists in studying derivatives of this class is understandable. A large number of investigators have studied the Fischer reaction. As long ago as 1910, Arbuzov and Tikhvinskii showed that this reaction can be catalysed by additions of copper, zinc, or platinum chlorides[370,371]. By using this reaction, N. N. Suvorov developed a method of synthesis of a known root formation stimulator for plants—3-indolylbutyric acid. Suvorov's work played an important part in establishing the mechanism of the Fischer reaction[372,373].

Kost and Yudin found that δ-ketonitriles can take part in the Fischer reaction and, depending on the conditions, nitriles of the indole or indolenine series are obtained[374].

These authors developed an elegant method for the synthesis of lilolidene structures by the scheme[375]:



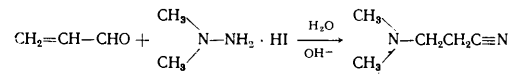
Grandberg developed an original method for the synthesis of important biogenic amines from arylhydrazones and γ-carbonyl compounds; an example is the synthesis of tryptamine[376]:



Of the other methods for building the indole ringe mention can be made of the work of Terent'ev and Grinev on the development of the Nenițescu reaction[344].

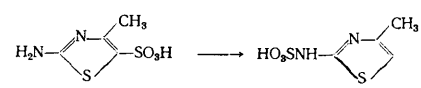
The extensive investigations of Kochetkov, Khomutova, and Sokolov were devoted to a study of isoxazole derivatives[377]. Electrophilic substitution in the izoxazole series was studied for a great number of examples.

A. N. Kost and I. I. Grandberg made a great contribution to the chemistry of heterocyclic derivatives of hydrazine. They developed a method for the synthesis of pyrazolines from azines, methods of dehydrogenating pyrazolines to pyrazoles[378], after which systematic investigations were begun into the chemistry of pyrazole[379]. Grandberg's investigations of the basicity of pyrazole systems include a series of general rules for the transfer of electronic influences through a pyrazole ring and the study of the influence of various factors (including conformational) on the conjugation of unsaturated groupings[380]. In papers of Ioffe and Zelinin[381] and also Grandberg the rearrangement of pyrazolines into nitriles was described; it is known in the literature as the "aminonitrile rearrangement"[382]. An example is the reaction of acrylaldehyde with dialkylhydrazines[383]:

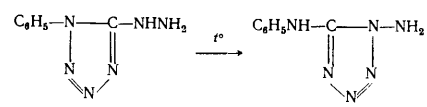


Several papers have dealt with the limits of applicability of this rearrangement[381-384]. Grandberg investigated the rules affecting the course of the reaction with breaking of the N–N bond and showed the genetic relationship of the aminonitrile rearrangement with other reactions of hydrazine derivatives[384].

I. Ya. Postovskii made an large contribution to the chemistry of heterocycles with two heteroatoms. He made a detailed study of the sulpho-derivatives of thiazole, and during this found an interesting example of the isomerisation of aminosulphonic acids into sulphaminic acids[385]:



Postovskii discovered the unique reaction of thermal isomerisation of 5-hydrazino-1-phenyltetrazole into aminoanilinotetrazole by the scheme[386]:



There are also the studies of Grinshtein and Chipen on aminotriazoles[387]; Mushkalo on benzothiazine, thiazoline, and thiazolidine[388]; Elina and Magidson on *N*-oxides of quinoxaline and pyrazine[389]; and Zhiryakov on thienothiazole and thienopyrrolenine[390].

The chemistry of natural products and their analogues was begun in the investigations of A. E. Chichibabin, V. M. Rodionov, I. L. Knunyants, and N. A. Preobrazhenskii. We will note in this connection the studies of Knunyants, Chelintsev, and Magidson on the synthesis of antimalarial substances[391,392], and the synthesis of Vitamin B_1 by Chelintsev and Benevolenskaya[393].

The synthetic chemistry of natural products was broadly developed in the studies of N. A. Preobrazhenskii and his students (R. P. Evstigneeva and N. K. Sarycheva). The work on the synthesis of pilocarpine, begun by A. E. Chichibabin, was successfully finished by the complete synthesis of this

compound[394]. Later Preobrazhenskii was the first to effect the complete syntheses of emetine, cinchonamine, curarine[395], and to create the industrial methods for the production of arecoline, cocaine, and pilocarpine. Work on the synthesis of important triglycerides of vegetable oils (linseed, soybean, cocoa bean oil) was developed on a wide front. These investigations led to the development of methods for the synthesis of saturated and unsaturated fatty acids (lauric, linolic, linoleic, arachidonic). A series of phosphatides and plasmogens entering into the composition of the brain and spinal cord was obtained from them[396].

N. A. Preobrazhenskii and R. P. Evstigneeva's work on the synthesis of porphyrins is of special interest. The authors developed original synthetic approaches to the synthesis of compounds of this type and began to study the natural chromoproteins[397]. Industrial methods of synthesising Vitamins A, B_1, B_2, B_6, PP, and E were developed under N. A. Preobrazhenskii's leadership.

In the field of vitamin chemistry (apart from the work noted above) mention must also be made of Berezovskii's investigations[398].

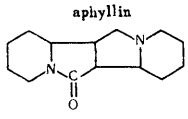
The work in the terpene field is directly connected with the use of turpentines and galipot, A. E. and B. A. Arbuzov[399] and Pigulevskii[400] made extensive investigations into the composition of turpentines.

The catalytic rearrangement of pinene into camphene, discovered by Tishchenko, gave a possibility of organising the production of camphors from turpentine[401].

We have already noted the work of S. S. Nametkin and his students on skeletal rearrangement. Extensive investigations in the terpene field were carried out by B. A. Arbuzov, who discovered the rearrangement of pinene into alloöcimene, and, with Z. G. Isaeva, studied the properties of terpenic α-oxides in detail; B. A. Arbuzov conclusively established the structure of levopimaric acid[402].

A great range of investigations into alkaloid chemistry was reached in the work of A. P. Orekhov and his students. In these studies about eight hundred native alkaloid-bearing plants were examined, from which about fifty new alkaloids were isolated[403]. The structure of a significant proportion of them was established, and in several instances was confirmed by synthesis. The structure and pharmacological value of the alkaloid anabasine, first isolated by Orekhov and Men'shikov[404,405], are generally known. Of the other alkaloids, we note aphylline, lupinine, convolamine, and salsoline[405,406]:

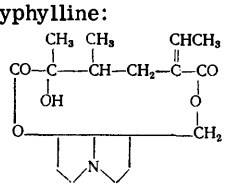
aphyllin



salsolin



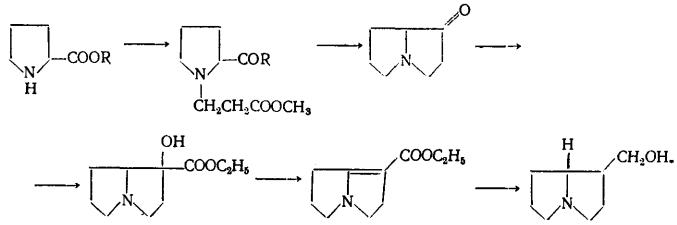
Especially interesting investigations were made by A. P. Orekhov and his student G. P. Men'shikov in the field of alkaloids of the heliotridane group. As was established by the work of these investigators, the alkaloids heliotrine, trichodesmine, platyphylline, etc. are derivatives of nitrogen-free branched unsaturated hydroxy-acids and alcohols of the 1-methylpyrrolizidine[407]. We give as an example the structure of platyphylline:



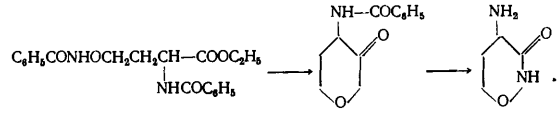
Investigations of alkaloids have been successfully carried out in the Uzbek SSR by Yunusov and Sadykov. A. S. Sadykov isolated about 100 alkaloids from the plants of Central Asia, about half of these for the first time; he made extensive investigations in the field of synthesis of alkaloids and the establishment of their structure. We mention also the series of studies by Sadykov into the reactivity of bipyridyls[408].

However, there has been an especially intensive development of the chemistry of natural compounds in the last decade. This found expression in the creation of the Institute for the Chemistry of Natural Compounds (IKhPS) and in the organisation of the journal "Khimiya Prirodnykh Soedinenii" [Chemistry of Natural Compounds]. The work of two schools is of the greatest value here: those of N. K. Kochetkov and M. M. Shemyakin.

N. K. Kochetkov dealt with most diverse problems of the chemistry of natural compounds. Thus, Kochetkov and A. M. Likhosherstov developed methods for the synthesis of pyrrolizidine bases and acids, entering into the composition of the heliotridane series of alkaloids. An example is the synthesis of isoretronecanol effected by these authors[409,410]:



In the studies of Kochetkov, Khomutov, Karpeiskii, Budovskii, and Severin[411] methods were developed for the synthesis of cycloserine and its analogues with the aim of studying the connection between structure and physiological activity of this antibiotic. As a result of the study of the mechanism of physiological action of cycloserine it was shown that it is a powerful inhibitor of the enzymes of nitrogen exchange, the co-enzyme of which is pyridoxal phosphate. Physiological activity is also exhibited by homocycloserine, which was synthesised by the scheme[412]:



The mechanism of the physiological action of this antibiotic was subsequently studied in greater detail by Khomutov[413].

A large series of papers by N. K. Kochetkov is devoted to carbohydrate chemistry. On the one hand work in the field of monosaccharide chemistry developed over a wide front. Thus, Kochetkov studied the problems of the bromination of monosaccharides by complexes of bromine with phosphorus(III) derivatives and hence found an original approach to the production of deoxysugars[414]. Kochetkov and O. A. Chizhov found a new analytical method for determining monosaccharides with the use of fragment mass spectrometry. The combination of this method with that of the methylation with trideuteriomethyl iodide enabled the sequence of bonds in oligosaccharides to be established[415,416]. Undoubtedly this method has great prospects for finding the structure of oligo- and poly-saccharides.

Of the work in the polysaccharide field we note the investigation of Kochetkov and Derevitskaya on the isolation and

characteristics of the polysaccharides of the group of substances present in blood[417].

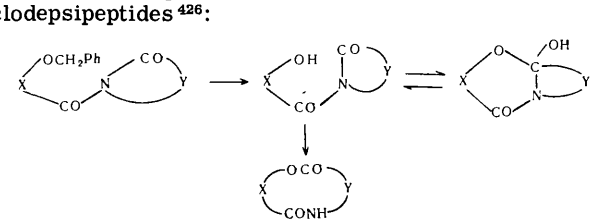
Many of the papers of N. K. Kochetkov and his coworkers (A. Ya. Khorlin, V. E. Vas'kovskii, Yu. S. Ovodov, O. A. Chizhov, and A. V. Bochkov) concern the study of natural glycosides. The first studies dealt with the isolation and establishment of the structure of the oligosides of Manchurian aralia [*Aralia mandschurica* Rupr. et Max. (Ed. of Translation)][418,419]. Kochetkov and G. B. Elyakov began the work on the isolation and characteristic of the ginseng [Panax ginseng C. A. Mey (Ed. of Translation)] alkaloids. G. V. Elyakov and coworkers have recently isolated glycosides (named panaxosides A–G) from gin seng roots, have established their main structure, and for several of the panaxosides have studied their detailed structure. It has been found that the panaxosides are oligosaccharides with 5–9 monosaccharide residues and a genin–panaxdiol–terpineol dammaranic series[420]. Now G. B. Elyakov, V. E. Vas'kovskii, and Yu. S. Ovodov have investigated physiologically active compounds isolated from marine organisms.

In conclusion we will note the work of Kochetkov and Budovskii on the chemistry of the nucleic acids[421]. Methods were developed for the selective splitting of heterocyclic nuclei entering into the composition of the nucleic acids (hydroxylamine method) which enabled original chemical approaches to studying the structure of these important biopolymers to be found.

The first studies of M. M. Shemyakin and his school in the field of the chemistry of natural compounds were devoted to the synthesis of the antibiotic levomycetin. The synthesis of racemic levomycetin—sintomycin—forms the basis for the industrial production of this antibiotic[422,423]:

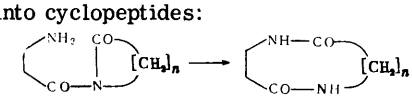
$$NO_2C_6H_4COCH_2NH_2 \cdot HCl \rightarrow NO_2-C_6H_4-\underset{NHCOCHCl_2}{\underset{|}{COCHCH_2OH}} \rightarrow NO_2C_6H_4\underset{OH}{\underset{|}{CH}}-\underset{NHCOCHCl_2}{\underset{|}{CHCH_2OH}} \cdot$$

The series of papers by Shemyakin, Ovchinnikov, and their students deals with the depsipeptides[424,425]. The first direction is connected with the synthesis of natural antibiotics depsipeptides (the enniatins A, B, C, sporidesmolide, *o,o'*-diacetylserratomolide, etc.), and inter alia for some of them earlier formulae were corrected. There was also a very interesting study of the influence of conformational factors on the cyclisation of depsipeptides[425]. The second direction (M. M. Shemyakin, V. K. Antonov, and A. M. Shkrob) is connected with the study of oxacyclols. In these authors' research it was found that oxacyclols obtainable by the spontaneous isomerisation of *N*-hydroxyacylamines and sometimes existing in tautomeric equilibrium with them, are capable of irreversible isomerisation into cyclodepsipeptides[426]:



where X = CH_2 or $[CH_2]_2$; Y = $[CH_2]_3$, $[CH_2]_4$, $[CH_2]_5$, or $[CH_2]_{11}$.

The azacyclols formed as a result of the isomerisation of *N*-aminoacyl-lactams are unstable and spontaneously are converted into cyclopeptides:



Possibly the rearrangements of the hydroxy- and aminoacylamides are some of the possible methods for the biosynthesis and transformation of peptides and depsipeptides.

A long series of papers by M. M. Shemyakin, M. N. Kolosov, and their students (Yu. A. Berlin, I. G. Bolesov, and V. V. Onoprienko) is connected with the establishment of the structure of antibiotic substances. Several years' investigations into syntheses[427] in the tetracycline field culminated recently in the complete synthesis of this antibiotic[428]. In the studies of this group methods were developed for the isolation and purification of antitumour and antivirus antibiotics of microbial origin—olivomycin, aburamycin, abicaviromycin, and the structure of some of them was established completely. In their studies these investigators discovered important relations between the structure and activity of a series of antibiotics and alkaloids, and showed the active centres and structural elements of the molecules which secured the biological activity at the cell and sub-cell levels. We note also the method developed by M. N. Kolosov for the synthesis of the analogues of chloroamphenicol. Here mention must also be made of Khokhlov's work on the isolation of new antibiotics[429].

We record also the work of V. P. Kucherov and coworkers (Gurevich, Grigor'ev, Serebryakov) on the development of methods for the isolation and synthetic modification of the gibberellins[430].

In the studies of Si. Zav'yalov and his coworkers (V. I. Gunar, M. P. Unanyan, and E. P. Gracheva) isoprenoids (for example, phytol) and homosteroids were synthesised from dihydroresorcinol. By use of the Deakin–West reaction the biogenetically similar synthesis of desthiobiotin was effected. Methods were developed for the synthesis of thymine, orotoic acid, 6-methyluracil, and 1,3-oxazines, the direct amination of uracils was achieved, and the selective *N*-glycosidation of silver salts of uracils[431,432].

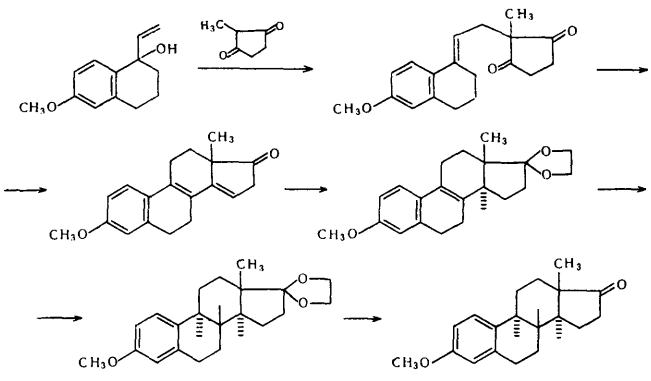
The study of amino-acids, polypeptides, and proteins has been greatly developed in our country. Synthetic investigations in the field of amino-acids is connected in principle with the problem of artificial food. Among these studies we will note the investigations of Feofilaktov[433], Terent'ev[434], and Belikov[435].

The work in the protein field was begun in the USSR by Zelinskii, Sadikov, and Gavrilov[436,437]. The present investigations in this field deal with the most varied aspects of this problem, starting at the synthesis of peptides and ending with the problems of the biosynthesis of protein; a detailed examination of these studies is impossible within the space allotted to the present review. We will only note the work of Kaverzneva[438] and Khurgin[439] on the kinetics of certain hydrolytic conversions of peptides, that of Botvinnik and Avaeva in the field of peptides containing hydroxyamino-acids[440,441], those of Stepanov in the field of pepsin[442], that of Silaev and Poddubnaya on antibiotics of a peptidal nature[443,444], that of Poroshin and Shibnev[445], and also Debabov in the field of peptides isomorphous with collagen[446].

Mention must be made of the work of Prokof'ev, Shabarova, and Bogdanov[477] in which various aspects of the nucleic acid chemistry were examined, and problems of the protein–nucleic acid bond were dealt with. In a long series of studies Prokof'ev and Shvachkin succeeded in synthesising various pyrimidylamino-acids (including natural ones)[448].

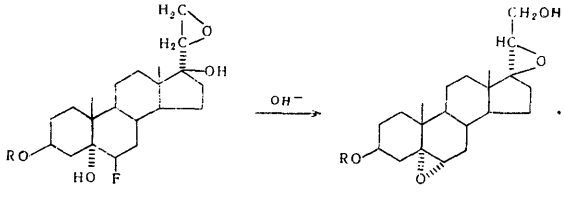
As already mentioned above, the first studies in the field of steroids were undertaken by I. N. Nazarov. These were continued by Torgov and his students Ananchenko, Leonov,

and Zakharychev[449-451]. The greatest achievement of this group must be considered to be the complete synthesis of oestrone from vinylmethoxymethyltetralol by the scheme:



This method of synthesising oestrone also achieved recognition abroad, as is shown by the work on its subsequent improvement and introduction, carried out in the USA, Federal Republic of Germany, and Japan. We note also that some of the intermediate compounds in this synthesis can be used for the synthesis of other steroidal compounds, and in particular, the heart aglycones.

Interesting investigations in the steroid field were made by A. A. Akhrem and coworkers (A. V. Kamernitskii, I. G. Reshetova, V. N. Dobrynin, and A. M. Moiseenkov). In the studies of this group the interesting migration of an oxide ring under alkaline conditions was discovered[452], the stereochemistry of the Favorskii rearrangement was studied by the example of steroidal dibromoketones[453], new reactions were found for the closing of epoxide rings in the steroid series, and methods were developed for the synthesis of highly active analogues of steroids with a broken ring B[454,455]. As an example we will give an interesting migration of the epoxide ring in alkaline medium[455]:



The great development of the boundary regions with inorganic chemistry is characteristic of modern organic chemistry. This is connected with the great practical value of organoelemental materials, and, in particular, fluoro-organic compounds and organosilicon materials, with the exceptional importance of organometallic compounds for synthetic purposes, and with their important use as catalysts for the most varied processes, including polymerisations. We must mention the development of the production of organometallic antidetonators, of selective organophosphorus fluorinating agents, of highly effective insecticides, of organosilicon and fluoro-organic heat-resistant materials, rubbers, and synthetic fibres. Organometallic compounds are of great significance for theoretical investigations. Even in the last century A. M. Butlerov and A. M. Zaitsev extensively used organozinc and organomagnesium compounds for synthetic purposes; in the prerevolutionary period P. P. Shorygin discovered important reactions for metallation. A. E. Arbuzov is rightly considered a pioneer in the field of the organic chemistry of phorphorus.

However, the greatest development in organoelemental chemistry occurred only in the thirties and forties and has continued to develop explosively to the present day. The fundamental achievements in this field and essentially also the creation of the enormous divisions of the chemistry of organoelemental compounds are connected with the school of A. N. Nesmeyanov, who has raised a great pleiad of students, among whom we can mention O. A. Reutov, N. K. Kochetkov, R. Kh. Freidlina, A. E. Borisov, I. F. Lutsenko, L. G. Makarova, L. I. Zakharkin, K. N. Anisimov, V. A. Sazonova, E. G. Perevalova, N. A. Vol'kenau, T. P. Tolstaya, N. S. Kochetkova, M. I. Rybinskaya, S. P. Gubin, V. N. Drozd, Yu. A. Ustynyuk, and A. V. Grib.

Great achievements in this field are linked with the school of K. A. Kochetkov, among whose students were M. M. Nad', N. I. Sheverdina, T. S. Talalaev, A. P. Skoldinov, and N. N. Zemlyanskii.

The broadest investigations in the field of phosphorus chemistry were undertaken by A. E. Arbuzov's school: G. Kh. Kamai, A. N. Pudovik, A. I. Razumov, V. S. Abramov, K. V. Nikanorov, and N. I. Rizpolozhenskii; by the school of M. I. Kabachnik: T. A. Mastryukova, S. T. Ioffe, V. A. Gilyarov, K. V. Matsuro, A. E. Shipov, and N. N. Godovikov; and also by the school of A. V. Kirsanov.

The chemistry of fluoro-organic compounds is rightly connected with the name of I. L. Knunyants and his students: B. L. Dyatkin, L. S. German, Yu. A. Cheburkov, G. A. Sokol'skii, and R. N. Sterlin.

Organic derivatives of almost all the elements of the Periodic System have been investigated by Soviet scientists to some extent.

Extensive investigations in the field of organoelemental chemistry embracing a considerable part of Mendeleev's Table have been made by the foremost Soviet organoelemental chemist, A. N. Nesmeyanov. Of course many of his investigations extend beyond the boundaries of organoelemental chemistry and concern general questions of organic chemistry, and many of these have been considered above.

One of the principal directions of Nesmeyanov's work is the development of a new method for the synthesis of organometallic compounds on the basis of binary diazonium salts. This reaction, which appears in all the textbooks and bears the name of its discoverer, was successfully used for the synthesis of the most varied derivatives of mercury, tin, lead, bismuth, thallium, arsenic, antimony, and zinc[456-458]:

$$(ArN_2X)_m \times MX_n + \frac{2m}{p} \times M' \rightarrow Ar_mMX_{n-m} + \frac{m}{p} M'X_p + N_2 .$$

The mechanism of the decomposition of binary diazonium salts in the presence of reductants has been studied and it has been shown that these processes are homolytic in nature and constitute one of the most important paths for the development of the chemistry of free radicals and homolytic processes.

Nesmeyanov and coworkers (L. G. Makarova and T. P. Tolstaya) investigated the possibility of using the heterolytic decomposition of diazonium salts for synthetic purposes. The investigation of this type of decomposition of diazonium salts gave results far removed from the framework of organometallic chemistry and led to the creation of new types of organoelemental compound with unusual valency.

In this way diarylchloronium, diarylbromonium, and triaryloxonium salts were obtained[459-462]:

$$C_6H_5N_2BF_4 + C_6H_5Cl \rightarrow (C_6H_5)_2Cl \cdot BF_4 + N_2 ,$$
$$C_6H_5N_2BF_4 + C_6H_5Br \rightarrow (C_6H_5)_2Br \cdot BF_4 + N_2 ,$$
$$C_6H_5N_2BF_4 + C_6H_5{-}O{-}C_6H_5 \rightarrow (C_6H_5)_2O \cdot BF_4 + N_2 .$$

Study of the chemical properties of the latter and in particular, the orientation in electrophilic substitution (nitration takes place in the *para*-position) led to the hypothesis of a new "oxane" valence state for the oxygen atom[463-465]. The results of an investigation of the mechanism of decomposition of the salts of aromatic onium compounds[466] are of great interest.

Subsequently Reutov and Ptitsyna developed a method for the synthesis of organic compounds of bismuth, tin, mercury, and antimony through diaryliodonium salts[467,468].

A. N. Nesmeyanov showed that on reaction with metal salts aliphatic diazo-compounds could form organometallic compounds[469-471]. For example, the reaction between diazoacetic ester and mercury(I) chloride is[469]:

$$4N_2CH_2COOC_2H_5 + 3HgCl \rightarrow 2CH_2ClCOOC_2H_5 + Hg(CCl{-}COOC_2H_5)_2 + N_2 .$$

Diazomethane reacts with mercury salts to give various products according to the ratio of the reagents[470,471]:

$$CH_2N_2 + HgX_2 \rightarrow XCH_2HgX \xrightarrow{CH_2N_2} XCH_2HgCH_2X .$$

Subsequently, studies of Braz, Yakubovich, and Ginsburg showed that this reaction is general—halogeno-derivatives of arsenic, antimony, bismuth, thallium, etc. were obtained[472,473].

Another method for the synthesis of onium compounds based on an exchange reaction was developed by Nesmeyanov, R. Kh. Freidlina, and E. M. Brainina. Thus the reaction of *trans*-di-2-chlorovinylmercury with iodine trichloride leads to dichlorovinyliodonium salts[474].

An interesting group of compounds is those provisionally termed "reverse onium compounds", where the multivalent atom is part of the anion, not the cation. Thus Nesmeyanov and Sazonova developed the synthesis of tetra-arylboric acids by the scheme[475]:

$$4RMgX + KBF_4 \rightarrow [R_4B]K + 4MgXF .$$

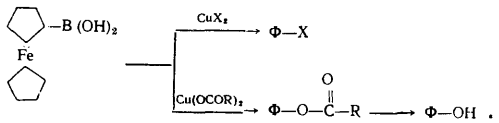
The compounds obtained are of interest as analytical reagents.

Nesmeyanov and coworkers[476-478] developed general methods for obtaining titanium compounds of the general formula $(RO)_nTiX_{4-n}$, where $n = 1, 2, 3, 4$, and X = Cl, Br; obtained titanium(III) compounds in the pure state, and obtained lower polyalkoxytitanoxanes.

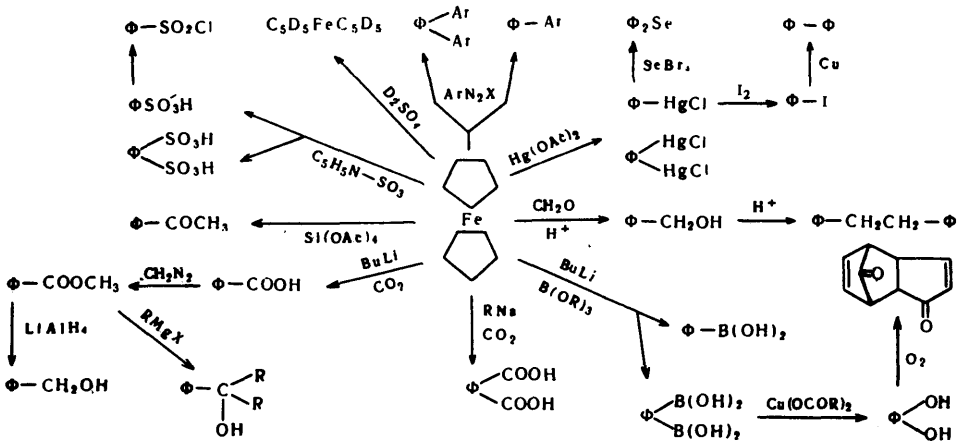
A. N. Nesmeyanov studied the reaction of chelate compounds of iron, zirconium, etc.[479]

As is well-known, the discovery of ferrocene heralded a flood of work in the field of π-complexes, deepened our knowledge of the nature of the chemical bond, and stimulated work on the ligand field theory and also synthetic investigations in the field of metal carbonyls. In our country the main studies in this region are connected with A. N. Nesmeyanov. Nesmeyanov, Perevalova, Gubin, and Ustynyuk began extensive investigations into ferrocene chemistry[480,481]. Scheme 3 shows the results of the studies of the reactions of aromatic substitution in the ferrocene nucleus.

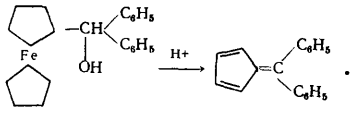
Nesmeyanov and Gubin[482] studied the oxidation potentials of ferrocene derivatives which enabled them to show the nature of the transfer of electronic effects through the ferrocene nucleus, In a series of papers Nesmeyanov, Perevalova, and Ustynyuk studied the influence of the ferrocene nucleus on the stabilisation of neighbouring carbonium, carbanionic, and radical centres[483]. The principal results were obtained by A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd. The elegant use of ferrocenylboric acids led to the production of such basic derivatives as hydroxyferrocene and halogenoferrocenes by the scheme[484]:



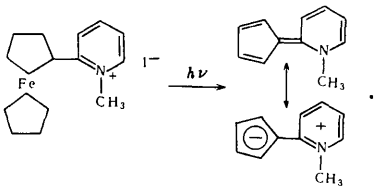
Scheme 3



These investigators studied ferrocenyldiazonium salts, nitrogen derivatives of ferrocene[485]. In studying ferrocenyldiphenylmethanol it was shown that the decomposition of the ferrocene to the fulvene by the following scheme is possible in principle[486]:



Nesmeyanov and Sazonova found a unique reaction of the photochemical decomposition of the ammonium derivatives of ferrocene by the scheme[487]:



Subsequently Nesmeyanov undertook extensive investigations of other types of π-complexes and in particular the π-complexes of palladium of σ- and π-bound cyclopentadienyl derivatives of various elements[488-490].

A. N. Nesmeyanov and K. N. Anisimov made extensive investigations into the synthesis of derivatives of metal carbonyls. Thus methods were developed for synthesising the carbonyls of chromium, molybdenum, and tungsten. Mixed carbonyls with two metal atoms in the molecule were synthesised, for example, $(CO)_5Mn-Re(CO)_5$ [491] and also some π-complexes, for example, π-cyclopentadienylcarbonylironchlorogermane by the scheme[492]:

$$\pi\text{-}C_5H_5Fe(CO)_2Cl + HGeCl_3 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2GeCl_3 + HCl$$

and cyclopentadienyldicarbonylniobiumtolane[493].

Of the works of other authors we note the investigations of Ya. K. Syrkin and I. I. Moiseev in the field of the π-complexes of palladium[494]. Of special interest are the investigations of M. E. Vol'pin and V. B. Shur in which the bonding of nitrogen by use of metallic π-complexes was shown to be possible in principle. For example, in the reaction of nitrogen with phenyl-lithium and cyclopentadienyl derivatives of titanium ammonia is obtained[495,496].

The work of Vol'pin and Shur give a powerful impulse to the investigation of the most diverse aspects of the chemistry and physical chemistry of molecular nitrogen; inevitably these ideas were immediately taken up and are being vigorously developed by a large number of investigators both in the USSR[497] and abroad[498].

K. A. Kocheshkov carried out extensive investigations in the field of organoelemental compounds. His first studies were made with A. N. Nesmayanov and concerned the extensive synthetic possibilities of the Nesmeyanov reaction. Kocheshkov's subsequent work was extremely varied and touches on many elements of the Periodic System. Thus, Kocheshkov and Sheverdina[499] made a detailed study of the metallation of aromatic hydrocarbons already discovered by Shorygin. It is interesting that a method was developed for the direct introduction of thallium into aromatic compounds[500]:

$$CH_3OC_6H_5 + Tl[OOCCH(CH_3)_2]_3 \rightarrow n\text{-}CH_3OC_6H_4Tl[OOCCH(CH_3)_2]_2 + (CH_3)_2CHCOOH.$$

Kocheshkov and Nesmeyanov studied a large number of reactions of double exchange of organometallic compounds; these reactions are a convenient method for making organoelemental compounds from readily accessible organomercury compounds[501-503]. Individual organomagnesium compounds were obtained in this way[503].

Sheverdin and Kocheshkov isolated individual mixed organozinc and organocadmium compounds and studied their properties in detail[504]: Kocheshkov and coworkers made a detailed study of organolithium compounds[505,506], on which basis an elegant method was developed for the synthesis of primary amines by the scheme[506]:

$$2RLi + CH_3ONH_2 \rightarrow R{-}NHLi + RH + CH_3OLi\ .$$

We note also the work of Kocheshkov and Zemlyanskii on the synthesis of plumboxanes and stannoxanes[507].

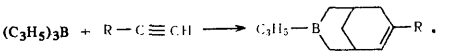
The interest in boron derivatives is due to the ever-increasing practical use of its derivatives. Undoubtedly there is also theoretical value in the chemistry of boron especially for dealing with problems of the nature of the chemical bond.

The greatest progress in boron chemistry was obtained, in the works of L. I. Zakharkin and coworkers (V. I. Stanko, O. Yu. Okhlobystin) and of B. M. Mikhailov and coworkers (Yu. V. Bubnov, V. A. Dorokhov, L. S. Vasil'ev).

In the studies of Mikhailov's group a path was developed for the synthesis of various derivatives of boron(III): trialkyl- and triaryl-borons, various oxygen-, sulphur-, and nitrogen-containing derivatives[508-511]. The study of mutual interchanges between different classes of organoboron compounds led to the discovery of the catalytic influence of the B–H bond on the exchange of radicals at the boron atom[510,511].

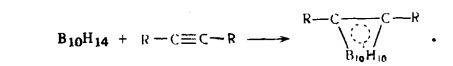
In Mikhailov's work great attention was paid to the study of the complex-forming ability of organoboron derivatives, with extensive studies of borenium and boronium compounds[508,512,513], neutral complexes, inner complexes[514,515], and also the effect of radicals at the boron atom on complex formation.

Special emphasis must be placed on certain aspects of the use of boron compounds in organic synthesis. Thus, extensive study of the derivatives of diborane, mercaptoborane, and aminoboranes made it possible to develop convenient methods for the synthesis of diols, alkenes with a known position of the double bond, and methylenecyclanes[516]. Of especial interest is the new reaction found by Mikhailov and Bubnov between triallylboron and acetylene[517]:



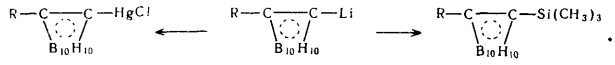
Study of the allyl derivatives of boron showed that these compounds exhibit reversible "valency isomerism" (proceeding according to the scheme of the allyl rearrangement)[518].

Zakharkin and coworkers synthesised some interesting compounds from acetylene derivatives and decaborane—they belonged to the group of carboranes, barene, and its derivatives[519]:

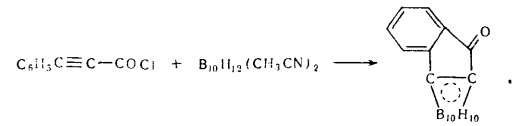


Barene has a high thermal stability; it is stable in relation to the action of alkalis and acids. It has been shown that the barene nucleus exhibits a pronounced electron-withdrawing effect: it hinders electrophilic addition to unsaturated derivatives and makes possible the metallation of the C–H bond[520,521]. A long series of papers by this group

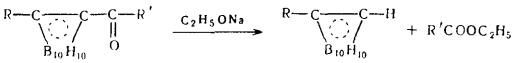
of investigators was concerned with the metallation of barenes. The carbonisation of Grignard reagents gave barenylcarbonic and acetic acids. From the lithium derivatives they synthesised a series of organoelemental compounds of the barene series containing phosphorus, silicon, tin, and mercury [520-523]:



An interesting property of disubstituted barenes is the ease with which intramolecular cyclisations take place. For example, the reaction of phenylpropynoyl chloride with bis(acetonitrile)decaborane(12) gives a cyclic ketone by the scheme [522,523]:

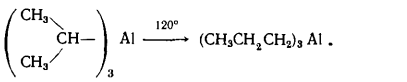


By the examples of esters of barenedicarboxylic acids and barenyl phenyl ketones it was shown that under the action of sodium ethoxide a C–C bond is broken [524,525]:



From the other studies of this group we note the work of Zakharkin and Strunin on the synthesis of organomagnesium compounds in ether-free media [526].

The chemistry of organoaluminium compounds has also been investigated by L. I. Zakharkin and O. Yu. Okhlobystin. For example, they made a detailed investigation of the reducing properties of di-isobutylaluminium hydride [527], and studied the exchange reactions between trialkylaluminiums and halides of mercury, phosphorus, boron, and lead [528,529]. These authors discovered the interesting reaction of the thermal isomerisation of isoalkylaluminium compounds into compounds with a straight chain [530]:

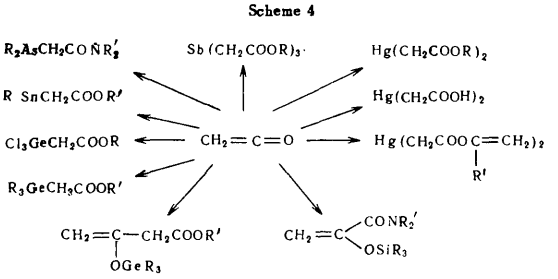


Of the elements of Group IV (of course, excepting carbon) the organic chemistry of silicon has been most developed.

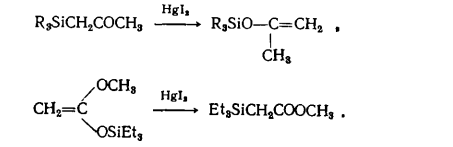
K. A. Andrianov can with justice be called the founder of the chemistry of organosilicon compounds in the USSR. Andrianov and his school studied problems of the synthesis of organosilicon monomers, ways of converting them into polymers, investigation of the properties of the polymers and materials based on them. Under Andrianov's guidance methods were developed for the vapour-phase synthesis of alkyl- and aryl-chlorosilanes, and also the theory of this process. The investigations of Andrianov and his school embrace the problems of the formation of polyorganosiloxanes of various types, the discovery of the laws of the formation of organosilicon polymers and oligomers, the study of hydrolytic polycondensation, the catalytic polymerisation of derivatives of inorganic rings and the establishment of mechanisms of these reactions, and the study of the physicochemical, mechanical, and dielectric properties of the polyorganosiloxanes. Andrianov and coworkers made extensive investigations into the synthesis of polymers with inorganic chain molecules which include (in addition to oxygen and silicon atoms) atoms of aluminium, boron, titanium, tin, phosphorus, and nitrogen. Andrianov and Khananashvili [531] examined theoretically the problem of the possibility of constructing polymers with inorganic chain molecules; they found the factors which influence the ability of the elements to form inorganic rings, framed with organic or organoelemental groups. The investigations of Andrianov and his school formed the basis for the creation of the organosilicon compounds industry.

Extensive investigations in the field of organoelemental compounds of Group IV were made by I. F. Lutsenko and his students (Yu. I. Baukov, V. L. Foss, S. V. Ponomarev, M. A. Kazankov, and Z. V. Kraits). They showed the great possibilities for the synthesis of various derivatives of silicon, germanium, and tin on the basis of keten, diketen, and enol acetates of carbonyl compounds [532-535]. They studied the conversions shown in Scheme 4.

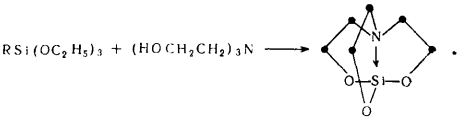
Scheme 4



In continuation of the earlier work of A. N. Nesmeyanov and I. F. Lutsenko mentioned above, a detailed study was made of the dual reactivity of α-mercurated and α-stannated compounds. This resulted in the production of a series of organoelemental *O*- and *C*-derivatives of vinyl esters of carboxylic acids, vinyloxysilanes, and phosphoric and phosphonic acids. Especially important results were obtained for derivatives of silicon and phosphorus, since here success was achieved in observing the conversion of the *O*- and *C*-forms. The greatest interest is in the isomeric conversions of organosilicon derivatives of acetone and methyl acetate, catalysable by mercury(II) iodide, which were discovered by Lutsenko and Baukov [535]:



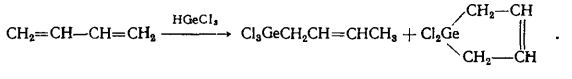
M. G. Voronkov completed successful investigations in the field of the chemistry of "atranes"—unique cyclic systems containing in a ring an atom of an element and a nitrogen atom. Silatranes are readily obtained by the reaction [536]:



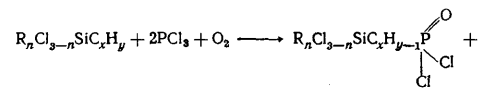
It is interesting that these compounds exhibit a definite physiological activity. In addition to silatrane, Voronkov and coworkers have synthesised boratrane, alumatrane, etc. [536].

A general property of all the "atranes" is strong coordination between the nitrogen and element atoms.

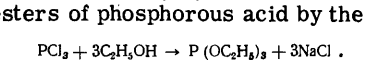
V. F. Mironov made extensive studies of the addition of silicon and germanium hydrides to unsaturated compounds [537,538]. Of especial interest is the reaction of trichlorogermane with dienes, leading to cyclic compounds [539]:



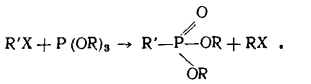
We note also the work of E. A. Chernyshev on the synthesis of compounds containing silicon and phosphorus [540]:



The chemistry of organophosphorus compounds was successfully developed in Kazan' by A. E. Arbuzov, B. A. Arbuzov and their students. As long ago as 1903 A. E. Arbuzov synthesised esters of phosphorous acid by the reaction:

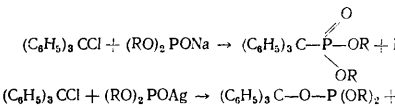


By studying the reaction of alkyl halides on the compounds he had obtained, A. E. Arbuzov discovered the rearrangement which bears his name [541]:



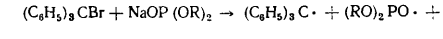
This reaction has proved to be one of the most important synthetic methods in organophosphorus chemistry. It has been used in the synthesis of esters of alkylphosphonic and dialkylphosphinic acids, phosphonocarboxylic acids, phosphonoketones, mixed oxides of tertiary phosphines, etc.; over 700 examples of this rearrangement have now been described [542,543].

A. E. Arbuzov and B. A. Arbuzov made a detailed study of the reaction of the metallic derivatives of dialkyl phosphites with triphenylmethyl halides. This reaction proceeds differently depending on the metal and halogen [544,545]:

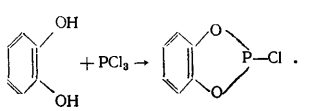


In addition, there are the studies of A. E. and B. A. Arbuzov on the structure of the so-called "Boyd's acid chloride". Of the two structures ascribed to this compound, $(C_6H_5)_3CPOCl_2$ and $(C_6H_5)_3COPCl_2$, the former was selected on the basis of a detailed experimental investigation.

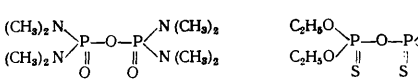
In studying the conversions of "Boyd's acid chloride", A. E. Arbuzov and B. A. Arbuzov developed an interesting method for obtaining free radicals according to the scheme [544,545]:



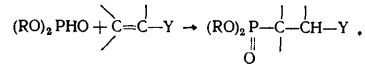
Some of the most interesting directions in A. E. Arbuzov's investigations are the synthesis of cyclic esters of phosphorous acid. A particularly detailed study was made of catecholphosphorochoridite, readily obtained by the reaction [546]:



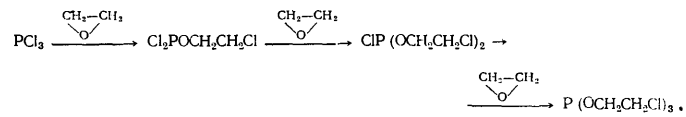
A large group of investigations by A. E. and B. A. Arbuzov are concerned with derivatives of pyrophosphoric acid [547], and are highly active insecticides. They include the well-known agricultural poisons "Oktametil" and "Ditiofos":



New preparations for the treatment of glaucoma ("Armin", "Fosarbin") were obtained. Of the relatively new achievements of the Kazan' school we will mention the discovery by B. A. Arbuzov and A. N. Pudovik of the addition of dialkyl phosphites to unsaturated compounds with an activated multiple bond; this reaction has been extensively studied by Pudovik and coworkers [548,549]:

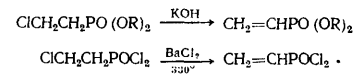


An original development in the chemistry of organophosphorus compounds occurred in the work of M. I. Kabachnik and his students, who found that the reaction of ethylene oxide with phosphorus(III) chloride leads to the synthesis of chloroethyl derivatives of phosphorous acid by the scheme [550]:



In subsequent papers, both of Kabachnik and of other authors (G. Kamai), the general nature of this reaction was demonstrated. On the basis of the chloroethyl derivatives various phosphorus(V) compounds were obtained (with the aid of the Arbuzov rearrangement).

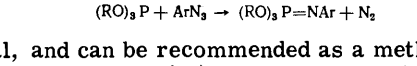
There is general interest in the production of esters of vinylphosphonic acid [551]:



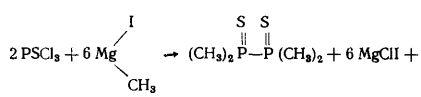
The vinyl compounds obtained are interesting as monomers for the production of incombustible polymers.

In Kabachnik's investigations chloromethyl derivatives of phosphonic acids were obtained [552], esters of α-ketophosphonic acids were studied [553], and the synthesis of organothiophosphorus compounds by the reaction of phosphorus sulphides with alcohols was investigated [554].

Kabachnik and Gilyarov showed that the reaction of aryl azides with phosphorus(III) derivatives, which proceeds by the scheme [555]:



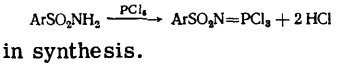
is general, and can be recommended as a method for determining phosphorus(III). We note also that the reaction for the preparation of tetramethyldithiodiphosphyl found by Kabachnik and Shepeleva [556]:



is now the best method for the synthesis of compounds of the tetra-alkyldithiophosphyl series.

Kabachnik has recently carried out extensive investigations on conjugation in non-coplanar systems containing phosphorus, and in particular, in phosphazocyanines [557].

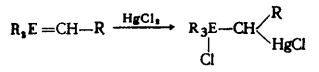
Mention must also be made of the work of Kirsanov and Derkach on the synthesis of trichlorophosphazosulphonaryls and trichlorophosphazocyls [558,559]:



and their use in synthesis.

G. Kamai has studied the chemistry of organoarsenic compounds [560]. There is also the work of O. A. Reutov and N. A. Nesmeyanov on the yields of arsenic and phosphorus [561]. In these studies it was found that the yields readily add

mercury(II) chloride to form unusual addition products, which exhibit "quasicomplex properties":



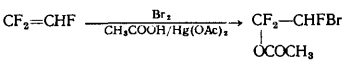
These compounds are fairly stable and may find applications in syntheses as "conservation" Wittig reagents.

We will mention also the systematic studies of E. G. Nifant'ev on methods of phosphorylation of polyols, monosaccharides, and polysaccharides [562].

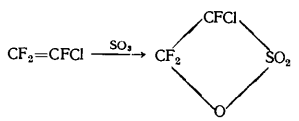
The greatest developments in the organic chemistry of fluorine have been in the research of I. L. Knunyants and his students [563,564]. The main direction of the work of this school was connected with showing the reactivity of fluoroalkenes, in studying the nature of the double bond in fluoroalkenes and the mutual influence of the groups in fluorinated derivatives of the most diverse classes. The rules for the electrophilic and nucleophilic addition in the fluoroalkene series were studied for a wide range of compounds.

There is special interest in the work of Knunyants and his students (B. L. Dyatkin, L. S. German, Yu. A. Cheburkov, and G. A. Sokol'skii) on the chemistry of fluoroacrylates, the chemistry of perfluoronitroso- and perfluoronitrocompounds, and on the study of reactions involving conjugated addition to fluoroalkenes.

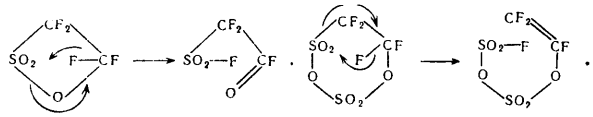
For example, Knunyants and his coworkers showed that hydrogen-containing alkenes, such as $CF_3CH=CH_2$ or $CF_2=CHF$ react with bromine in acetic acid in the presence of mercury(II) acetate or sulphate to form bromohydrins [565]:



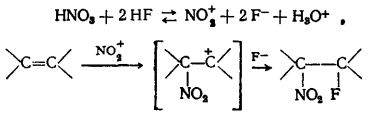
Fluoroalkenes readily add sulphur trioxide to form cycloaddition products of β-sultones [566]:



The development of the chemistry of fluorinated sultones led to the discovery of interesting isomerisations, which probably proceed through a "bicyclic mechanism" [567]:



I. L. Knunyants has made extensive studies of the nitrofluorination of fluoroalkenes, which proceeds by the scheme [568]:



This reaction was first effected by Titov by the example of tetrafluoroethylene [569].

It is impossible to omit the work of Knunyants and Sterlin on the synthesis and investigation of the properties of perfluorovinylmercury [570].

Of the other work in this field we note the investigations of I. V. Martynov and Yu. L. Kruglyak on the nitration of fluoroalkenes by a sulphuric–nitric acid mixture [571] and that of A. Ya. Yakubovich's study of nitrosation [572].

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Obviously, within the framework of a journal article it is impossible to review thoroughly all the great achievements of Soviet organic chemists. However, even in this brief survey the enormous attainments of Soviet scientists in the most diverse branches of science are evident. This guarantees future progress in organic chemistry in our country.

1. A.E.Chichibabin, R.A.Konovalov, and A.A.Konovalova, Zhur.Russ.Fiz.-Khim.Obshch., 53, 193 (1925).
2. B.A.Arbuzov, in Collected Papers, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Goskhimizdat, Moscow, 1954, Vol.3, p.7.
3. A.E.Arbuzov, in "Trudy Sessii AN SSSR po Organicheskoi Khimii" (Proceedings of the Sessions of the Academy of Sciences of the USSR on Organic Chemistry), 1939.
4. A.N.Nesmeyanov and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 14 (1942).
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FIFTY YEARS OF SOVIET PHYSICAL CHEMISTRY

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The Soviet period in the development of physical chemistry in our country is characterised by an extremely rapid increase in the volume of scientific research and in the number of specialised scientific topics investigated.

The appearance of the physicochemical laboratory underwent a radical change. The Soviet generation of physical chemists has witnessed on more than one occasion an almost complete technical re-equipment of its laboratories, brought about by the impact of modern experimental methods borrowed from physics, electronics, and computer science. The interface between physical, organic, inorganic, and analytical chemistry is now almost completely blurred. Physicochemical methods and concepts have become predominant in the study and interpretation of the results obtained in fundamental studies of every aspect of chemical science.

The rapid and fruitful penetration of the theoretical and experimental methods of modern physics concerns practically every problem in physical chemistry (structure of matter, valence theory, chemical equilibria, kinetics and mechanism of chemical change, problems in photochemistry and radiation chemistry, electrochemistry, semiconductor chemistry, theory of heterogeneous catalysis, chemistry of surface phenomena, colloidal chemistry). In the last fifty years, important advances have been made in all these fields, and many of the most important fundamental ideas of chemistry have had to be revised. The close association of organic and inorganic chemistry with physical chemistry (the "chemification" of physical chemistry) has given rise on the one hand to the appearance of new and rapidly developing branches of science such as physical organic chemistry, and on the other hand to the far-reaching penetration of mathematics into the whole of theoretical and applied chemistry. This tendency has become even more marked as a result of the increasing use of modern computing techniques.

Significant advances in the principles and methods of industrial chemistry have been both the result and the motivation of the development of physical chemistry. New methods of carrying out chemical reactions were quickly introduced into the chemical industry: these include the separation and purification of liquids and gases, sorption techniques, new and versatile continuous catalytic processes, and definite progress towards the rational control of chemical reactions including the development of chemical cybernetics. The physical chemistry of surface phenomena, electrochemistry, and radiation chemistry are helping to solve important technical problems, such as the development of new methods of preparation of disperse materials, the conversion of chemical into electrical energy, and problems in radiation-chemical synthesis. The growth of physical chemistry has been of tremendous importance also in the polymer field. The present review will not deal specifically with this field, which has become a self-contained branch of modern chemistry.

If we compare the development of Soviet chemistry with that of the rest of the world we see that our Soviet science leads (or keeps pace with) the science and technology of advanced capitalist countries in many important branches of chemistry. These include chemical kinetics, the theory of catalysis, electrochemical kinetics, adsorption theory, physicochemical mechanics, combustion and explosion problems, and many others.

These important advances in physical chemistry cannot be understood otherwise than in the context of earlier developments in this science. It is well known that physical chemistry first arose in our country at about the time when chemistry began to claim the status of a science in its own right. Lomonosov was the first to propose the term "physical chemistry" for the branch of science which straddles the boundary between chemistry and physics, and gave the following definition of this scientific discipline: "physical chemistry is a science which explains in terms of the concepts and experiments of physics that which takes place in mixed bodies during chemical operations"[1]. Lomonosov also carried out the earliest experimental physicochemical investigations in the chemical laboratory of the Academy of Sciences, now inseparably associated with his name.

Nearly all the main sections of physical chemistry began gradually to take shape during the second half of the nineteenth century. The first ideas on catalysis were put forward, studies of chemical affinity began, progress was made in the study of electrochemical phenomena, heat effects accompanying chemical change were investigated, the universal gas law was established, the simplest laws of chemical kinetics were formulated, and above all the fundamental laws of thermodynamics were determined.

Physical chemistry experienced a particularly significant development during the period immediately preceding that discussed in the present review (from the 1880's to the 1920's). Much was accomplished during this period, particularly development in chemical thermodynamics.

During the nineteenth and especially the early twentieth centuries some higher scientific institutions in St. Petersburg, Moscow, Kazan', Kiev, Khar'kov, Yur'ev, and other cities had better laboratories than those of the Academy, and therefore the role of the Academy of Sciences in the development of chemistry (and in particular physical chemistry) was not so much to strengthen experimental research within its own walls as to stimulate the scientific life of the nation by electing leading scientists as Members, by sponsoring prizes, and by publishing scientific work[2].

After the Great October Socialist Revolution, following Lenin's instructions, the Academy of Sciences began a systematic study and survey of the natural industrial resources of Russia, and set up the first Chemical Institutes. At the same time, various subsidiary research institutes were founded, and some of these have played a major role in the development of Soviet physical chemistry[3,4].

At present, the most important physicochemical institutes of the Academy of Sciences are the Institute of Chemical Physics, the Institute of Physical Chemistry, and the Institute of Electrochemistry.

In May 1958 the Central Committee of the Communist Party of the Soviet Union issued important directives for the faster development of chemical industry and science. Since then, the Academy of Sciences has created and successfully developed a number of new physicochemical institutes. These include the Institute of Electrochemistry

of the Urals' branch, which specialises in the electrochemistry of fused salts and solid electrolytes, and also the Institutes of Catalysis and of Chemical Kinetics and Combustion of the Siberian Section of the Academy of Sciences of the USSR.

Many other institutes of the Academy have some involvement in physicochemical investigations: the Institute of Organoelemental Compounds, the Zelinskii Institute of Organic Chemistry, the Kurnakov Institute of General and Inorganic Chemistry, the Institute of High-Molecular-Weight Compounds, the Institute of Petrochemical Synthesis, etc.

Physicochemical studies at one of the oldest of the chemical institutes of the Academy of Sciences—the Radium Institute—also produced notable contributions. In 1961 this Institute was transferred from the Academy of Sciences to a different administration.

Foremost among the other physicochemical institutes are the Karpov Physicochemical Institute, the Pisarzhevskii Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, and the Faculty of Chemistry of Moscow State University.

The origin and the earliest development of chemical physics took place at the Leningrad Physico-Technical and Radiographic Institute (GFTRI) under the direction of A. F. Ioffe. In 1921, a small team led by N. N. Semenov was set up within the GFTRI to study electronic effects in chemistry[5]. This laboratory investigated electric fields, molecular physics, and electronic phenomena. Towards the beginning of 1931 the activities of the electron chemistry laboratory had progressed well beyond the scope of a section of a research institute. At about this time the whole of the scientific world had began to associate research in chemical physics with the name of Semenov and his coworkers. As a result of the phenomenal growth of the Leningrad Institute, the decision was made in September 1931 to reorganise it into a physico-technical scientific research complex, consisting of three independent research institutes. One of these institutes, opened on the 15th October 1931, was the Leningrad Research Institute for Chemical Physics. Since that day, having achieved independent status, the Institute of Chemical Physics (IKhF) has intensified its efforts towards its basic objective: to introduce the theories and methods of physics into chemistry, the chemical industry, and many other branches of the national economy.

The scientists of the Institute have gone a long way from the first researches, made thirty-five years ago, to the modern work in the most varied aspects of chemical physics. In 1939 the Institute was admitted into the Academy of Sciences of the USSR.

The branch of the Institute created in 1957 and staffed almost exclusively by young scientists is beginning to produce good results. The Institute is still directed by its founder, Nobel Laureate and Hero of Socialist Labour N. N. Semenov.

The Institute is now investigating the kinetics and mechanism of chemical reactions (chain reactions in particular), and the kinetics and mechanism of catalytic processes, chemical processes induced by penetrating radiations, at low and at high temperatures, under high pressures, etc. It is developing new processes and improving existing processes for the production of polymers and monomers, it is studying the degradation and stabilisation of polymers, it is developing new physical methods and apparatus for chemical investigations such as mass spectrometry, radiation spectrometry, the Mössbauer effect, etc. It is refining the theory of combustion and detonation processes in gaseous and condensed systems, studying the kinetics of biological processes, and applying physicochemical investigations to the mode of action of chemicals and of physical agents on various biological systems.

In 1967 the Institute of Chemical Physics was awarded the Order of Lenin for its achievements in the development of chemical physics and the training of specialists.

Another important centre of physical chemistry in the Academy of Sciences of the USSR is the Institute of Physical Chemistry. The history of this Institute goes back to 1930, when the Laboratory for Colloid Chemistry and Electrochemistry (LAKE) was set up at the initiative of V. A. Kistyakovskii[6]. In this laboratory, he and his pupils studied problems of metal corrosion, electrocrystallisation [electrodeposition], and flotation.

When the Academy of Sciences moved to Moscow in 1934 the Praesidium of the Academy reorganised the Laboratory into an Institute for Colloid Chemistry and Electrochemistry (KEIN), with a more comprehensive research programme. In addition to the above topics, the Institute undertook problems in colloid chemistry, the physicochemical dispersion of metals, the theory of lubrication, the formation of metallic coatings, and several others.

V. A. Kistyakovskii was the director of these establishments until 1939, when he was succeeded by A. N. Frumkin, whose main activities had previously been centred at the Karpov Physicochemical Institute and Moscow State University.

In 1945 the Institute of Physical Chemistry (IFKh) was created from the Institute for Colloid and Electrochemistry.

From 1949 until 1953 the Institute of Physical Chemistry was directed by G. V. Akimov. During this period the Corrosion Section, led by Akimov, grew rapidly.

At the moment the following topics are being pursued at the Institute: the physicochemical mechanics of metals, concrete, and colloidal systems; the forces acting close to phase boundaries and in thin films; the formation and precipitation of aerosols; the thermodynamics and kinetics of sorption on carbon and mineral sorbents, and chromatography; the protection of metals against corrosion; the preparation of polymer coatings. Problems in radiochemistry and radiation chemistry also claim a significant part of the effort of the Institute.

Since 1953 V. I. Spitsyn has been the director of the Institute as well as leader of the work on radiochemistry.

In 1958 the Institute of Electrochemistry (IELAN), based on the Electrochemistry Section of the Institute of Physical Chemistry, was created on the initiative of A. N. Frumkin in response to the need for more extensive work on electrochemical kinetics (the theoretical basis of the most important practical applications of electrochemistry).

In the 1950's some problems of major importance to the national economy and demanding an increased effort in the field of electrochemical kinetics began to be clearly recognised. These include the realisation of electrochemical power sources (fuel cells) able to convert the chemical energy of a fuel directly and continuously into electrical energy; the development of electrochemical transducers

for automation, control, and guidance systems having a number of valuable properties, especially the ability to operate at low frequencies; the provision of methods of electro-synthesis of organic compounds offering very pure products; and various other problems.

Investigations are now proceeding at the Institute in the following directions: the theory of electrochemical processes and the structure of the metal/electrolyte interface; the electrochemistry of organic compounds; the mechanism of processes in electrochemical power sources (particularly fuel cells), in electrochemical transducers, and in the electrochemical machining of metals; surface phenomena on semiconductors (including organic semiconductors); the mechanism of radiation processes; the quantum theory of chemical reactions; physicochemical hydrodynamics and its application to the theory of technological processes.

Since its foundation the Institute has been directed by A.N. Frumkin, Hero of Socialist Labour and president in 1965–66 of the Comité International de Thermodynamique et de Cinétique Électrochimiques (CITCE).

The structure and reactivity of a wide range of organoelemental compounds are being investigated at the Institute of Organoelemental Compounds (INEOS). The Zelinskii Institute of Organic Chemistry (IOKh) is examining spectroscopically the molecules of organic compounds. Nearly half of the work of the Institute is directed towards a study of the catalytic interconversions of hydrocarbons. The Topchiev Institute of Petrochemical Synthesis (INKhS) is developing catalytic methods for converting hydrocarbons into valuable chemicals, and is working on plasma chemistry and on the physical chemistry of polymers. Work on the physical chemistry of the oriented state has reached an advanced stage at the Institute of High-Molecular Compounds (IVS). The Kurnakov Institute of General and Inorganic Chemistry (IONKh) is the principal centre in our country for the development of the field of research originated by Kurnakov: physicochemical analysis. This includes studies of the physicochemical properties of various groups of compounds, metals, salts, semiconductors, organic compounds, and also the conditions of equilibrium in multiphase systems. Extensive investigations are proceeding at the Institute on the structure of complex compounds of a great variety of metals, including the platinum, transuranium, and rare elements. At the Kazan' Institute of Organic and Physical Chemistry (IOFKh) work is directed towards electrochemical methods of metal treatment and the electrocrystallisation [electrodeposition] of metals.

The Karpov Physicochemical Institute was the first (and, until the 1930's, the only) institute in this country with a physicochemical objective. The Institute began operations in 1918 as the Central Laboratory of the Chemistry Section of the Supreme Economic Council (VSNKh). A.N. Bakh[7-9] was one of the founders of the Institute, which he directed continuously for 28 years.

Since those early years, Bakh has gathered together some talented young scientists, and has created, with the support of the Government, an ideally equipped institute whose scientists are continually striving towards linking science with technology.

A.N. Frumkin took an active part in developing the Institute as a physicochemical establishment, and was its Deputy Director from 1929 until 1947, when he was succeeded by V.A. Kargin. The present Director of the Institute is Ya.M. Kolotyrkin.

The leading physicochemical experimentation and the major theoretical advances for which the Institute was responsible have won the acclaim of scientists in the Soviet Union and abroad. During the pre-war period, the activities of the Institute were aimed mainly at three large sections of physical chemistry: surface phenomena and electrode processes, the structure of matter, and chemical kinetics and catalysis. Since the war, there has been a considerable increase in the effort devoted to polymer science and catalysis. Studies in radiation chemistry and in the separation of mixtures have grown into fields of study in their own right. Important problems solved at the Institute include the development of new processes and the improvement of existing processes for chemical technology.

The Karpov Institute has also undertaken a heavy load of organisational work to assist the development of Soviet physical chemistry. It has convened regular series of conferences and published physicochemical journals. The Institute still retains close links with the Academy of Sciences. Many dozens of scientists now working in our country have been trained at the Institute.

The Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR[10] was founded a few years after the Karpov Institute (in 1927), but it has also won a leading place among the Soviet institutes specialising in physical chemistry.

Much of the work of this Institute is devoted to studies, by ESR, infrared spectroscopy, and other methods, of the structure, reactivity, and transformations of free radicals formed during electrochemical reduction, and of the sterically stabilised radicals which act as oxidation inhibitors in polymers. Other activities include the mass-spectrometric and isotopic study of various organic reaction mechanisms, of the mechanism of oxidation of various ions by peroxides, of adsorption phenomena, of the mechanism of the radiation-induced and the oxidative degradation of polymers, and an ESR study of the kinetics of fast protolytic reactions.

Extensive developments have taken place in mechanistic and kinetic studies of industrial catalytic processes, and of the part played by macrokinetic factors, in relating catalytic activity to thermodynamic properties, in systematising and correlating data on catalysis with a view to developing a theory for the selection of catalysts.

Furthermore, the Institute is now successfully engaged in the following directions: the utilisation of solar energy, the use of nuclear radiations in chemistry, the synthesis of zeolites, and studies of sorption mechanisms.

Physicochemical investigations at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR have been highly significant: this applies particularly to the work on the thermodynamics and kinetics of complex-formation reactions and on the theory of chemical bonding in complexes (K.B. Yatsimirskii), on comprehensive studies of different problems in the electrochemistry of fused salts (Yu.K. Delimarskii), on colloidal chemistry, and on a number of other problems.

Many important physicochemical projects are being developed in the Academies of other republics of the Soviet Union: the electrodeposition of metals at the Academy of Sciences of the Lithuanian SSR (Yu.Yu. Matulis), heterogeneous catalysis and the theory of acids and bases at the Academy of Sciences of the Kazakh SSR (D.B. Sokol'skii and M.I. Usanovich), polymer mechanics at the Academy of Sciences of the Latvian SSR, the structure of inorganic

compounds at the Academy of Sciences of the Moldavian SSR, etc.

Among the institutions engaged in physicochemical research, a leading place belongs to the Chemistry Faculty of the Lomonosov Moscow State University [11,12]. The history of this faculty goes back to the creation, during the earliest years of Soviet rule (1919–1921), of a chemistry section of the Faculty of Mathematics and Physics, and to the organisation (in 1922) of a Scientific Research Institute for Chemistry within the University. The Chemistry Faculty of Moscow State University achieved independent status in 1929–1930.

In 1929 a Chair in Physical Chemistry was created as part of the Chemistry Faculty. This department grew quickly, and established a number of laboratories. By 1930–1932 it included the following laboratories: electrochemistry (A. N. Frumkin), contact processes for the heavy chemical industry (N. N. Petin), halurgy (A. V. Rakovskii), photochemistry (A. I. Rabinovich), and colloid chemistry (V. A. Naumov). Some of these laboratories eventually grew into independent departments.

When the Chemistry Faculty was organised, the Chair of Physical Chemistry was entrusted to A. V. Rakovskii. After his death (in 1941) it passed to A. V. Frost, and is now held by Ya. I. Gerasimov.

The Department of Physical Chemistry is a large scientific research establishment engaged in wide-ranging investigations into chemical thermodynamics and thermochemistry, catalytic reaction mechanisms, adsorption, molecular spectroscopy, colloid chemistry, the electrochemistry of gases, and electron diffraction studies of molecules. Other sections of the department are investigating the physical chemistry of disperse systems, electrochemical kinetics, the physical chemistry of high polymers, and chemical kinetics. Many of the sections are led by Academicians and Corresponding Members of the Academy of Sciences of the USSR. The Chemistry Faculty of the Zhdanov Leningrad State University is investigating ion-exchange theory (B. P. Nikol'skii), the thermodynamics of multicomponent systems and electrochemical kinetics. Physicochemical research is active also in other institutes of higher education such as the Mendeleev Moscow Institute of Chemical Technology, the Lomonosov Moscow Institute of Fine Chemical Technology, the Odessa State University, the Tomsk State University, etc.

Thus, in contrast to the pre-revolutionary period, physicochemical research is being carried out in large scientific complexes operating by a predetermined plan which reflects modern trends of research as well as the needs of the national economy, and not by individual scientists assisted at the most by a few coworkers.

In conclusion, we note that in recent years the network of physicochemical journals has grown appreciably (but less so than in the advanced capitalist countries). Before the war only two specialist physicochemical journals were published in our country: Zhurnal Fizicheskoi Khimii and Kolloidnyi Zhurnal, as well as the foreign-language publication Acta physicochimica USSR (which ceased to exist in 1946). Now, in addition to these, we have Elektrokhimiya, Khimiya Vysokikh Energii, Zhurnal Strukturnoi Khimii, Kinetika i Kataliz (the last two being published by the Siberian section of the Academy of Sciences of the USSR), and Zashchita Metallov (published jointly by the State Committee for Science and Technology, the Ministry of the Chemical Industry, and the Academy of Sciences).

Having briefly described the growth of the network of scientific establishments specialising in physical chemistry and their role in the overall scientific context, we shall discuss the major results obtained during the past 50 years. Through lack of space, this review must be a fragmentary one, and many important achievements have had to be omitted.

MOLECULAR STRUCTURE. REACTIVITY. QUANTUM CHEMISTRY. PHOTOCHEMISTRY

Soviet scientists are successfully investigating the relationship between the structure and the reactivity of molecules, the theory of elementary chemical processes and of energy-transfer processes, the theory underlying the application of radio-frequency spectroscopy (ESR and NMR) to the study of the structure and properties of matter, chemical spectroscopy, the Mössbauer effect, X-ray and electron diffraction, and the theory of molecular vibrations. In many of these topics important progress has been made in spite of the relatively small number of workers engaged.

Scientists of the Soviet Union have made outstanding contributions to developments in the chemistry of complexes, and to studies of their structural features. The foundations were laid by the work of L. A. Chugaev, who carried out systematic studies of the complexes of platinum metals even before the revolution [13]. Chugaev founded one of the leading schools of research on complexes. The able scientists who joined Chugaev (I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, N. K. Pshenitsyn, O. E. Zvyagintsev, and others) carried on the work of their teacher with outstanding success. They prepared hundreds of previously unknown complexes, studied their properties, and found practical uses for them. Chernyaev put forward the rule of the trans effect—an important generalisation of the influence of inner-sphere substituents in the coordination compounds. The trans effect concept gave a theoretical foundation to the development of multistage methods of preparation of complexes having a prescribed structure and configuration. Studies of the mutual effect of ligands (of which the trans effect is a special example) became the central theme of a great deal of chemical work in the USSR and abroad. The trans effect was demonstrated not only on platinum, but on many other elements: rhodium, cobalt, iridium, rhenium, etc. In ruthenium compounds the cis effect (first discovered by Grinberg) was investigated as well as the trans effect.

Grinberg and his coworkers were among the first to apply radioactive isotopes to the study of the structure and properties of complexes. Specially important results were obtained in their work on the kinetics of exchange between ligands and ions in solution.

Recent structural studies, carried out mainly at the Kurnakov Institute of General and Inorganic Chemistry, have added considerably to our understanding of the shapes (spatial structures) of complex ions of various metals. In particular, it was shown that the less usual polyhedra (coordination numbers five and seven) are fairly common among transition metals, and that frequently the structure is polymeric either due to bridging atoms or groups of atoms (halogens, oxygen, water, or hydrazine molecules, etc.) or due to metal–metal bonds (as in the acetato-complexes of univalent and bivalent rhodium and the halides of bivalent rhenium). These structural studies, together with the results of other physicochemical investigations, have identified and characterised some new types of chemical

bond (many-centre bonds in transition metal compounds, partial bonds, and particularly metal–metal bonds). Much valuable information on the structure of inorganic compounds was obtained in studies of the infrared spectra of coordination compounds.

The research on quantum chemistry led by Ya. K. Syrkin and M. E. Dyatkina deserves a special place among these investigations.

Syrkin was among the first in the USSR to undertake work on quantum chemistry and has developed it successfully up to the present time. His quantum chemical calculations of the energy and other properties of organic and inorganic compounds have led to many important predictions. He successively developed the theory of covalent bonds in inorganic compounds and the concept of covalent bonding in crystals which has proved so valuable in understanding the properties of semiconductors.

Much of Syrkin's effort was devoted to problems in the physics of the elementary chemical act. He put forward the original view that the elementary acts of many chemical reactions occur through five-, six-, or seven-membered rings with a sextet of electrons.

In recent years he has actively investigated the mechanism of reactions involving aromatic metal complexes (ferrocene, ruthenocene, etc..) and the π-complexes of some platinum group metals.

Dyatkina made a significant contribution to the theory of inorganic chemistry. She published many papers on the theory of directional valencies and the theory of the valency states of atoms in molecules. These include the most systematic investigation of the valency states of both transition and non-transition elements, from which many conclusions of the greatest importance in inorganic chemistry may be drawn.

Syrkin and Dyatkina developed the most satisfactory of the existing theories of aromatic and π-complexes of metals, and made a systematic study of the electronic structure of the tetrahedral oxo-anions of the transition metals.

A fundamental contribution to the application of the X-ray structural method to problems in inorganic chemistry, resulting in the development of crystal chemistry, came from N. V. Belov and his students (Institute of Crystallography of the Academy of Sciences of the USSR). They identified the structural units in silicates, explained the function of the cations, and computed a large number of complicated silicate crystal structures.

Since 1944, the Institute of Organoelemental Compounds led by A. I Kitaigorodskii has studied the packing of organic molecules in crystals. The concept of close packing of molecules, the principle of identifying the structure on that basis (the so-called "geometrical analysis"), and the symmetry rules following from the basic packing law—all these were rapidly adopted both in the field of low-molecular compounds and in the high polymer field. The laboratory developed improved physical methods for the structural investigation of organic and organoelemental compounds, originated and developed a new branch of crystal chemistry (organic crystal chemistry), proposed a method of quantitative conformational analysis, and is now successfully engaged on developing the basic aspects of the physics of organic crystals.

The same laboratory is carrying out wide-ranging investigations of the reactivity of organic and particularly of organoelemental molecules.

An extensive series of investigations by D. N. Kursanov on the chemistry of the carbonium ion, the mechanism of dehydration of alcohols, and the reactions of quaternary ammonium ions has shown that these processes involve a carbonium mechanism.

Other work by Kursanov on heterolytic reactions has dealt with hydride transition reactions. This work has made significant contributions to modern views on the hydride mobility of hydrogen in organic compounds.

The classical work of Kursanov on the reactivity of non-benzenoid aromatic systems is widely known.

Organometallic compounds have made possible a clear demonstration of dual reactivity in the absence of tautomerism. On this basis, M. I. Kabachnik drew a distinction between the phenomena of dual reactivity and tautomerism as equilibrium isomerism. He subsequently developed a quantitative theory of tautomeric equilibrium as an acid–base equilibrium, and discovered new experimental approaches to the study of these phenomena.

The work of R. Kh. Freidlina in new areas of organic chemistry has become widely known: it includes radical telomerisation and the regrouping of radicals in solution, as well as methods of synthesis based on these phenomena.

The simultaneous discovery by the Soviet physicists L. I. Mandel'shtam and G. S. Landsberg and by the Indian physicist Raman of the molecular light-scattering method was of incalculable importance in developing the science of the structure of matter. Thie method was widely used by B. A Kazanskii at the Institute of Organic Chemistry in studies on hydrocarbons.

A systematic investigation of the spectra of compounds having different combinations of atomic groups, by P. P. Shorygin of the Institute of Organic Chemistry, allowed him to establish the main rules which relate the spectra of molecules to the specific parameters of the chemical bonds and of the system of energy levels in a molecule. From these studies it has been possible to characterise the effect of substituents on π-bond systems as a function of the position of the substituent atom in the Periodic Table, of the type of intermediate units, of the orientation in space of the interacting groups, and of the chain length of the conjugated structural elements. A specific effect of heavy atoms contacting π-bond systems through an intermediate atom (oxygen, methylene, or other groups) has been discovered and investigated.

The work of A. N. Terenin[14] on the photodissociation of molecules has played a fundamental role. This worker was the first to put forward a correct model of the mechanism of the primary interaction of a quantum of light with a molecule. Terenin's work provided the foundations of the electronic theory of the structure and energetics of molecules. The classical papers by Terenin on the photochemistry of halide vapours are of fundamental importance to the basic problem of photochemistry—the mechanism of the primary elementary process. These investigations are attracting renewed interest in connection with the problem of a quantum light source.

Studies of compounds in the gas phase led to the discovery of various new phenomena: the "activation" of the fluorescence of complex molecules by adding other gases, and the effect of light gases (helium and hydrogen) on the intensity of absorption by complex gas molecules.

One of Terenin's students, B. S. Neporent, made an important contribution to the spectroscopy of complex mole-

cules: he proposed a rational physical classification based on intramolecular interactions of the various types of state (electronic and vibrational).

A series of papers by Neporent was devoted to spectral studies of intermolecular interactions in condensed media. He found a solution of the complicated problem of the influence of the solvent on the intensity of molecular spectra: this provided the foundations for the development of general methods of absorption spectral analysis.

M. V. Vol'kenshtein (Institute of High-Molecular Compounds, Academy of Science of the USSR) made a number of theoretical investigations of intensities in the infrared and Raman spectra of polyatomic molecules, of problems in rotational isomerism, and in the field of molecular optics. Some of Vol'kenshtein's work dealt with problems in quantum chemistry.

An important series of investigations into quantum chemistry was carried out recently in Sokolov's laboratory of the Institute of Chemical Physics. A quantum-mechanical model of the hydrogen bond was developed, an effective method was found for optimising approximate wave functions and the operators used to calculate various characteristics of atoms and molecules, and a simple and effective method was proposed for calculating the magnetic screening constants of nuclei in NMR spectra.

The study of elementary processes in gases led to the development of a theory of the thermal decomposition of molecules which takes account of the non-equilibrium nature of the process. Problems arising in the application of resonance spectroscopy in chemistry were investigated, and a useful method was developed for calculating the transition probabilities of spin–lattice relaxation for paramagnetic ions and radicals in solids.

Wide-ranging investigations of the structure and reactivity of molecules are in progress at the Moscow State University.

O. A. Reutov's team is working on a number of theoretical problems in organic chemistry, with special reference to organometallic compounds, and is using many physicochemical research techniques: the stereochemistry and kinetics of substitution reactions at a saturated carbon atom, the mechanism of free-radical reactions in the liquid phase, the mechanism of the synthesis of organometallic compounds, and many others.

The laboratory of V. M. Tatevskii is investigating the detailed relationship between the spectra and the structures of hydrocarbons of various classes, and is looking into some problems in the theory of molecular structure and in the dynamics and statics of molecular systems.

A. I. Shatenshtein (Karpov Institute) made a systematic study of the kinetics and mechanism of hydrogen exchange in non-aqueous solvents (NH_3, HF, etc.). The assumption underlying this work is the acid–base character of hydrogen exchange in solutions, with the postulate that hydrocarbons can take part in protolytic reactions with strong bases and acids.

The X-ray laboratory of this Institute (G. S. Zhdanov) has also made substantial contributions to our knowledge of the structure of matter and to our understanding of the nature of the chemical bond by systematic crystal-chemical studies of important groups of chemical compounds.

CHEMICAL KINETICS. THEORY OF COMBUSTION AND EXPLOSION PROCESSES

During the past few decades it has become clear that chemical reactions as a rule are complicated processes consisting of many elementary acts and proceeding with the participation of various frequently unstable intermediates. It is not surprising, therefore, that the scope of chemical kinetics should have begun to increase even in the 1920's, when workers began to seek out the laws controlling complex reactions, and the general features responsible for the peculiar course of the majority of chemical reactions. The young Soviet physical chemistry took an active part in the creation of the new chemical kinetics, achieving a position of leadership in a number of aspects [15].

The acknowledged centre of this work in the Soviet Union was the Institute of Chemical Physics, with its affiliated establishment. However, the ideas and methods of modern chemical kinetics spread far and wide to other institutes, both academic and affiliated, and also to university laboratories.

The largest contribution to the development of this branch of science came from the school of N. N. Semenov, who created the modern theory of chain reactions by unifying an enormous fund of experimental data. These were exhaustively explained by considering the relationship between the rates of the various processes involved in the mechanism of chain reactions (generation, propagation, branching, and breaking).

The results obtained in 1926 by Semenov's coworkers Yu. B. Khariton and Z. F Val't in their work on the quenching of luminescence in a mixture of phosphorus vapour and oxygen gave additional impetus to the development of the theory of chain reactions. New phenomena were discovered which transcended the scope of existing views on the mechanism of chemical change: these were the strikingly sharp transitions of reactive mixtures from a state of almost complete inertness to a violent reaction, accompanied by ignition.

To explain this phenomena Semenov put forward the concept of branching chain reactions, which quickly gained wide acceptance. If the number of chain-branching events is greater than the number of chain-breaking events, the reaction rate steadily increases due to the continuous appearance of new chains until ignition of the mixture of reactants sets in ("chain explosion"). Semenov proposed the idea of chain breaking at the walls of the reactor. The theory of chain breaking in the volume of the reactor was developed independently by Semenov and Hinshelwood.

Semenov and his coworkers (Yu. N. Ryabinin, A. V. Zagulin, A. A. Koval'skii, and others) discovered in 1928–1930 the existence of sharp explosion limits in the oxidation of sulphur vapour, hydrogen, carbon monoxide, and hydrogen sulphide, thus increasing manyfold the number of known examples of ignition and demonstrating the generality of branching chain reactions.

Besides the chain explosion process, another very important and common type of ignition is known: the so-called thermal explosion. This type of explosion is due to the disruption of thermal equilibrium in the system, leading to a progressive increase in the reaction rate until explosion sets in.

In 1928, Semenov published a quantitative theory of thermal explosion, as well as the theory of chain ignition,

entitled "Theory of Combustion Processes". In that same year A. V. Zagulin confirmed Semenov's formula relating the explosion pressure to temperature for a number of systems (explosion of chlorine dioxide, explosion of hydrogen/chlorine mixtures, etc.), thus demonstrating the correctness of the thermal explosion theory. Semenov's monograph "Chain Reactions", published in 1934 in the Soviet Union and in 1935 in England, was based on the whole of this work. The book treats the massive array of existing experimental data on the kinetics of gas-phase reactions (and some liquid-phase reactions) from the point of view of the theory of chains [16,17].

In the years that followed, research on chemical chain reactions reached enormous proportions both in our country and abroad. Among the workers at the Institute of Chemical Physics, M. B. Neiman and his coworkers produced extensive evidence that the oxidation of hydrocarbons involves a degenerate branching mechanism. Neiman also examined in detail the two-stage ignition of organic compounds; the essential feature is that hydrocarbons, aldehydes, alcohols, etc., often burn in two stages: the cold flame stage and the hot flame stage. Mention must also be made of the work of A. A. Koval'skii and M. V. Polyakov on homogeneous–heterogeneous reactions and of Koval'skii's localised calorimetric method, which enabled him to show that many catalytic reactions begin at the catalyst surface but continue in the gas phase, where they follow a chain mechanism. A. B. Nalbandyan demonstrated that branching chain reactions can be controlled by controlling the rate of heterogeneous chain breaking; with N. M. Emanuel' and others he also investigated homogeneous catalysis in oxidations and many other reactions. The work on the influence of catalytically active additives on the initial stages of chain oxidations in the gas or the liquid phase has revealed new methods of controlling chemical processes under industrial conditions.

More recently, new and useful concepts have appeared in this work, such as the stimulation of slow branching chain oxidations, which make use of the self-accelerating and self-maintaining properties of branching chains.

In joint work by Nalbandyan and members of the Institute for the Chemical Industry, homogeneous catalysis was used to develop a new technological approach to the production of formaldehyde by the oxidation of natural gas.

Chain theory had been formulated on the basis of formal kinetics: it still needed additional chemical foundations. It was essential to establish the nature of the active centres in chain reactions and of the elementary processes which constitute the mechanism of a chain reaction, and to measure the rate constants of these processes. Only by the application of the newer physical methods could these problems be solved. For a number of years, V. N. Kondrat'ev and his coworkers have been developing various methods of this type which allow free atoms and radicals to be studied under the conditions existing during a chemical reaction (the spectroscopic resonance, absorption method, the catalytic recombination method). By these methods it was shown that OH radicals and H atoms are present in the combustion zone of hydrogen, carbon monoxide, and other gases at the appropriate concentrations for flame conditions. These active particles were shown to play an essential role in the development of the reaction. The rate constants of the elementary processes involving OH radicals and H atoms were measured, and in this way a full quantitative description of a branching chain reaction was obtained: the oxidation of hydrogen, a model gas-phase oxidation reaction. A monograph by A. B Nalbandyan and V. V. Voevodskii gives a detailed quantitative analysis of this reaction.

Voevodskii introduced the concept of the role of heterogeneous factors in the theory of the cracking of alkanes. This allowed him to explain a number of difficulties encountered by the generally accepted theory of Rice. As a result of his work on the structure and properties of free radicals, he discovered a new type of free-radical reaction and put forward a quantitative theory of the cracking of alkenes. In his studies of the recombination of atomic hydrogen on catalytically active surfaces, Voevodskii identified two régimes under which this process can take place: a high-temperature and a low-temperature régime; he also measured the recombination efficiency on metallic and oxide catalysts. These results, combined with a number of theoretical generalisations, led to the realisation that heterogeneous–catalytic reactions can occur by a mechanism analogous to the chain mechanism.

V. I. Gol'danskii made a detailed study of the general theory of tunnelling transitions in chemical reaction kinetics assuming both maxwellian and quantum energy distributions of the reacting molecules.

These, and many other investigations on a variety of reactions of different classes of compounds, have produced convincing evidence that, as suggested by Semenov in his book, chain reactions are of common occurrence.

Furthermore, even in 1939–1940 (in the year following the discovery of the fission of atomic nuclei by Hahn and Strassmann), N. N. Semenov's coworkers Yu. B. Khariton and Ya. B. Zel'dovich had published the first essentially correct theory of the uranium fission chain reaction.

The mass spectrograph was used for the first time ever to solve a problem in chemical kinetics in V. N. Kondrat'ev's laboratory. As a result of the work of V. L. Tal'roze, the mass spectrometric method is now widely used to study complex chemical mixtures and processes.

S. Z. Roginskii and his coworkers were among the first (together with A. I. Brodskii of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR) to use labelled atoms in chemical kinetics.

The use of polarography to investigate molecular intermediates in complex chain reactions has thrown light on the mechanism of many oxidations of organic compounds (V. Ya. Shtern and coworkers).

Nowadays, new methods are used to study the mechanism of electronic processes: the electron spin resonance and the nuclear magnetic resonance method, and gamma-resonance spectroscopy (V. V. Voevodskii, V. I. Gol'danskii, L. A. Blyumenfel'd, V. B. Kazanskii, and others).

The electron spin resonance method, discovered by the Soviet physicist E. K. Zavoiskii at Kazan', has become standard all over the world for the detection and structural investigation of free radicals formed as reaction intermediates or in other ways.

The Institute of Chemical Kinetics and Combustion of the Siberian Section of the Academy of Sciences of the USSR is extensively studying the kinetics and mechanism of chain and radiation-chemical reactions. The kinetics of chemical change in gaseous and condensed media are being investigated.

M. G. Gonikberg is making interesting studies in the field of chemical kinetics at the Institute of Organic Chemistry.

This work is mainly aimed at the effect of pressure on the rate constants of liquid-phase reactions. One of the most important results obtained is the conclusion, based on extensive experimental data, that the accelerating effect of pressure increases as the reaction becomes more sterically hindered. The reason for this is the partial overlapping of the van der Waals spheres of the atoms which screen the reaction centres in the activated complex: thus, additional compression becomes possible during the formation of the activated complex. These results were the basis of a proposed new method for studying the structure and properties of the transition state and the mechanism of organic reactions by kinetic studies at high pressure.

Beginning in the second half of the 1950's, many investigations have been devoted to the kinetics of polymerisation processes. Lack of space compels us to mention only a few of these.

The pioneer in this field was S. V. Lebedev, who studied the kinetics of the polymerisation of diene and allene hydrocarbons in the late 1920's.

S. S. Medvedev and his school (Kh. S. Bagdasaryan, A. D. Abkin, A. R. Gantmakher, and others) made an important contribution to studies of polymerisation processes. By treating polymerisation on the basis of chain reaction theory they put forward the fundamental view that polymerisation processes occur through free radicals. This led to an understanding of the chemical nature of the elementary stages of polymerisation and copolymerisation processes.

Much effort was devoted in Medvedev's work to the kinetics of anionic and cationic polymerisation, and also to coordination polymerisation of hydrocarbon and polar monomers.

Some important contributions to polymerisation kinetics were made by B. A. Dolgoplosk, whose scientific output was aimed primarily at the chemistry of synthetic rubber. In particular, much of his work was connected with the oxidation–reduction initiation of radical chain polymerisation, cross-linking, and degradation processes in polymers.

V. A. Kargin and his school are widely known for their fundamental studies of the structure and properties of polymers in a condensed phase and in solution. During the past 10 years Kargin, working in the Department of High-Molecular-Weight Compounds of the Chemistry Faculty of Moscow State University and at the Institute of Petrochemicals Synthesis, has carried out studies aimed at finding new methods of synthesis of macromolecules and at controlling polymerisation processes. This work was largely based on the methods of chemical kinetics.

In recent years, studies of the kinetics of polymerisation processes have attracted a great deal of attention at the Institute of Chemical Physics.

A detailed study of the kinetics and mechanism of the ionic polymerisation of monomers containing a heteroatom, made in the laboratory of N. S. Enikolopov, led to the discovery of a new elementary act (chain transfer with chain breaking).

At the same Institute, N. M. Chirkov has been studying since 1958 the polymerisation and copolymerisation processes of alkenes on complex catalysts. A. A. Berlin demonstrated, in his studies of the three-dimensional polymerisation of oligoacrylates, the essential role of the relative decrease in the chain breaking and chain growth constants with increasing viscosity of the medium during the course of the reaction.

Investigations of combustion and explosion processes are closely linked with work in the field of chemical kinetics. Scientists from the Academy of Sciences made important contributions to the development of this area: these include the thermal theory of flame propagation (developed by Ya. B. Zel'dovich, D. A. Frank-Kamenetskii, and N. N. Semenov, 1939–1948) and the theory of detonation developed by Zel'dovich in 1940. The thermal theory of combustion is the most systematic in taking account of the kinetics of the chemical reaction at the combustion front, of the heat transfer processes, and of diffusion. In some of the simplest examples the thermal theory gives a simple analytical expression for the rate of normal combustion, which is a great advance over alternative theories of flame propagation and allows the main rate-determining factors of normal combustion to be identified. The thermal theory is also applicable to combustion in condensed systems: it was shown experimentally in the case of explosives (by A. F. Belyaev of the Institute of Chemical Physics, 1938) that combustion is preceded by evaporation or sublimation of the combustible condensed material.

The first contributions to the theory of turbulent combustion came from the Soviet school of physical chemistry.

The theory of detonation formulated by Zel'dovich is based on the assumption of negligible heat conduction during flame propagation by detonation, which implies a definite structure of the detonation wave front. Zel'dovich specially stressed the role of the chemical (kinetic) factor in the phenomenon of detonating combustion. An important instance of detonation (spherical detonation) was discovered by S. M. Kogarko, who also noted the broadening of the detonation limits in wide-bore tubes and made numerous contributions to safety techniques. Special combustion régimes were discovered and investigated by K. I. Shchelkin and his coworkers.

Comprehensive studies of the main characteristics of explosion and of explosives were published by V. K. Bobolev, P. F. Pokhil, A. Ya. Apin, F. I. Dubovitskii, and others.

At the same Institute, A. S. Sokolik and A. N. Voinov (1936) proposed and exhaustively investigated a new method of ignition of the fuel mixture in internal combustion engines: mixing-chamber flame ignition. This method offers a lower specific fuel consumption and considerable economy. At present, the Institute (L. A. Gussak) in cooperation with workers in industry has developed a new type of automobile mixing-chamber engine. The results of this work are being exploited in the motor-car industry of the country.

CATALYSIS

In the field of catalysis, Soviet science can claim important and universally recognised achievements.

Studies in catalysis developed in parallel with studies in other ancillary areas (chemical kinetics, thermodynamics, adsorption, solid-state theory).

At present, catalytic reactions form the basis of most modern industrial chemical and petrochemical processes, in particular large tonnage processes such as cracking and reforming, and the preparation of many products and intermediates of heavy organic synthesis by oxidation, dehydrogenation, dehydration, isomerisation, alkylation, dealkylation, etc. Studies of the reactions of hydrocarbons contained in natural gas or formed during petroleum refining are of great importance in present-day chemistry.

These investigations have given rise, during the last few decades, to a new branch of the chemical industry—petroleum chemistry, which is producing many hundreds of valuable products second to none in their practical importance.

The extensive development in a short time of this new branch of the chemical industry was made possible first and foremost by the vast scientific effort of the Soviet school of organic chemists working on catalysis under the direction of N. D. Zelinskii. The work of this school was wholly aimed at the catalytic conversions of hydrocarbons: the broad outlines of this work were very clearly described by Zelinskii in his paper read before the session of the Academy of Sciences in 1936, entitled "Contact Phenomena and Changes in the Chemical Nature of Hydrocarbons" [18]. Zelinskii's school included A. A. Balandin, B. A. Kazanskii, N. I. Shuikin, and later A. F. Plate, A. M. Rubinshtein, L. Kh. Freidlin, Kh. M. Minachev, R. Ya. Levina, M. B. Turova-Polyak, S. R. Sergienko, Ya. T. Eidus, and many others. The work of this school (mostly associated with the Zelinskii Institute of Organic Chemistry and Moscow State University) was largely devoted to the study of organic reactions. In this review we shall consider only the physicochemical aspects of this work.

One of Zelinskii's closest collaborators, Balandin, proposed and extensively developed the multiplet theory of catalysis, which to a considerable extent set the pattern of Soviet work in the field of organic catalysis. This theory (whose basic premises were published as long ago as 1929) [19] combines modern views on the structure of matter with the theory of the structure of organic compounds, and can satisfactorily explain the catalytic transformations of organic compounds. Balandin showed that the elementary catalytic act is possible only for some definite ratios of the interatomic distances in the reactant molecules and in the crystal lattice of the catalyst (structural correspondence principle). He also explained the role of factors such as the energy of the bonds which are formed and broken during the reaction, the adsorption potentials, and the heats of reaction (energy correspondence principle).

These principles enable us to take account of the specific features of a catalytic reaction and of the catalysts needed to carry it out, and offer the possibility of predicting the behaviour of a molecule on a catalyst surface.

Besides this work, Balandin and his coworkers also made substantial contributions to the study of the kinetics of heterogeneous catalytic reactions.

Among other activities at the Institute of Organic Chemistry on the physicochemical aspects of heterogeneous catalysis, we must mention first of all the work of A. M. Rubinshtein and his coworkers on the topochemistry of catalysts, on the influence of phase composition, degree of dispersion, and crystal lattice distortions on the catalytic properties and on the texture of catalysts, the detailed investigations of the origin of catalysts, and the work on developing methods of catalyst preparation, etc.

The work of Kh. M. Minachev and coworkers on the catalytic properties of rare-earth elements, and on the use of various types of synthetic zeolites as hydrocarbon isomerisation and alkylation catalysts, is also very important.

Another great theoretical achievement of Soviet scientists in the field of heterogeneous catalysis is the electronic theory. The pioneer of the emphasis on electronic aspects in Soviet physical and inorganic chemistry was L. V. Pisarzhevskii [20], to whom are credited the now familiar definition of oxidation as the loss of an electron, the earliest experiments on the effect of radiation on catalytic reactions, the suggestion that the electrons of the catalyst take part in the catalytic reaction, and the correlation of the electronic properties of solids with their catalytic properties [21].

The foundations of the electronic theory of catalysis were laid by S. Z. Roginskii. The theory states that electrons from the catalyst take part in oxidation–reduction reactions, and the catalytic activity is related to the electronic structure of the catalyst. It was an obvious development to proceed from the postulated link between the catalytic activity and the electronic structure of solids to a study of the semiconductor nature of catalysts. These developments led Roginskii (together with F. F. Vol'kenshtein) to the electronic theory of catalysis at semiconductors, and to the discovery (with O. V. Krylov) of new types of redox catalysts. The application of the electronic theory to the mild oxidation of hydrocarbons and to the ammonia synthesis has resulted in significant improvements in existing catalysts and in the possibility of further development in these important industries (Institute of Chemical Physics, Institute of Physical Chemistry).

The work of Roginskii and his collaborators (O. V. Krylov, L. Ya. Margolis, G. M. Zhabrova, and others) has established new rules relating the catalytic activity of solids to the position of their elements in the Periodic Table, and relating catalytic properties to semiconductor properties, to the peculiarities of the catalytic spectrum, and to the choice of catalyst.

Another important result associated with the name of Roginskii is his very recent proposal to carry out catalytic reactions in a chromatographic régime. In this method the catalytic conversion of the reactants in the reactor is combined with chromatographic separation of the products. Higher conversion efficiencies can be achieved than under normal conditions, and significantly lower reaction temperatures are possible. Furthermore, the desired product can be obtained in a higher state of purity. Subsequently, Roginskii and Yanovskii proposed a method for carrying out catalytic reactions in a pulsed chromatographic régime which allows catalysts to be assessed much faster on the laboratory and pilot-plant scale.

Another interesting aspect is the hypothesis put forward by N. N. Semenov, V. V. Voevodskii, and F. F. Vol'kenshtein that adsorbed free radicals have an important part to play in heterogeneous catalysis: the corollary is that catalytic reactions can proceed by a chain mechanism. Although it was subsequently shown that chain reactions are less common in catalysis than had originally been thought, the prediction was confirmed in a number of instances (compare the work of Ya. T. Eidus on the catalytically initiated hydropolymerisation of alkanes, Roginskii's work on the Fischer–Tropsch synthesis, etc.). However, the study of adsorbed free radicals has attracted a great deal of interest in recent years in connection with the extensive development of ESR work. In many instances it has been possible to examine in detail the structure and properties of adsorbed free radicals, and to demonstrate their key role in adsorption, catalysis, and radiation catalysis processes (V. B. Kazanskii).

Studies in the field of catalysis are developing successfully at the newly created Institute of Catalysis of the Siberian Section of the Academy of Sciences of the USSR, led by G. K. Boreskov.

Boreskov was responsible for fundamental investigations on the theory of catalysis and on the scientific foundations

of the practical application of catalytic reactions. He introduced the concept of specific catalytic activity and showed that this quantity is approximately constant for most catalysts. Using tracer techniques, he developed methods for measuring the energy of the bond between the reactants and the catalyst, and demonstrated the importance of this parameter in the prediction of catalytic activity, he published a number of major investigations of the kinetics of catalytic reactions, and he gave a general formulation of the importance of interactions between the reaction mixture and the catalyst.

The Institute has formulated the principles which control the preparation of catalysts with an optimum pore structure: as a result, a new catalyst for the production of sulphuric acid giving a twofold increase in reaction rate has been developed.

Studies of model reactions and of the optimisation of catalytic processes, aimed at shortening the time between laboratory investigations of catalytic reactions and industrial exploitation, claim a significant part of the work of the Institute.

M.I.Temkin (Karpov Institute) put forward the theory of reaction kinetics at inhomogeneous surfaces. He proposed a logarithmic adsorption isotherm (the Temkin isotherm) which is widely used all over the world in work on chemisorption, heterogeneous catalysis, and electrochemical kinetics. By using this isotherm, Temkin was able to derive theoretically valid kinetic equations for a number of industrial catalytic processes. The first example of the fruitful application of these ideas was the development of a theory for one of the most important processes of chemical technology—the synthesis of ammonia. Temkin also established the kinetics and the mechanism of other important processes, such as the conversion of carbon monoxide, the gasification of coal, isotope exchange, the oxidation of ammonia and ethylene, the hydration of acetylene, and the hydration of ethylene.

The work of Temkin on the kinetics of catalytic processes is being widely applied in the design of catalytic plant and in the optimisation of processes with the help of electronic computers. The flow-circulation method, which offers a number of advantages for experimental studies of the kinetics of heterogeneous catalytic reactions, was suggested by Temkin. His contribution to the development of the general foundations of the kinetics of multistage chemical reactions was also a major one.

Mention must also be made of the large effort at the Institute of Petrochemical Synthesis on thermocatalytic methods for refining petroleum and petroleum products (K.P.Lavrovskii) and on the catalytic production from petroleum hydrocarbons of higher fatty alcohols suitable for the preparation of wetting agents (A.N.Bashkirov and V.V.Kamzolkin).

In recent years the Institute of Physical Chemistry (P.A.Rebinder and E.D.Shchukin) has worked on the principles underlying the control of the mechanical stability of catalysts by applying the concepts of physicochemical mechanics. In particular, they were able to increase the strength of the bismuth–molybdenum catalyst used for the oxidative dehydrogenation of propene and butene.

During the period of Soviet rule, a large number of catalytic investigations was carried out at Moscow State University. In the mid-1920's E.I.Shpital'skii (followed by N.N.Petin and N.I.Kobozev) developed and established experimentally the theory of intermediate compounds in homogeneous catalysis. In 1939 Kobozev proposed the theory of active ensembles. The theory of the kinetics of reactions under flow conditions was developed by the work of A.V.Frost and G.M.Panchenkov. Frost and Panchenkov, with K.V.Topchieva, successfully investigated catalysis on alumina–silicas.

We cannot ignore the contribution of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR (A.I.Brodskii and V.A.Roiter) to studies of the mechanism of catalytic reactions by the tracer atom method, or that of the Kazakh University (D.V.Sokol'skii) to the development of continuous catalytic hydrogenation of vegetable fats at low temperatures.

Sokol'skii developed new methods of investigation and control for hydrogenation catalysts, and in particular he discovered an interesting new phenomenon: the sharp decrease in electrical conductivity of a catalyst moistened with solvent upon removing the adsorbed hydrogen.

All these researches, together with some others in the field of heterogeneous catalysis, provided a wealth of information on the kinetics of heterogeneous reactions and on methods for investigating these reactions, on the theory of topochemical processes, and on the statistics of non-uniform surfaces. Lastly, the calculations needed in industrial processes involving heterogeneous catalysis were greatly assisted by the original and intensive development of the macroscopic kinetics of heterogeneous processes in the USSR, including diffusion kinetics, physicochemical hydromechanics, the calculation of thermal régimes, and the theory of reactions in a fluidised bed (V.G.Levich, O.M.Todes, D.A.Frank-Kamenetskii).

The work of Levich was a fundamental contribution to this field of research: he even proposed the term "physicochemical hydrodynamics" for the branch of science which deals with the multiplicity of problems presented by the effect of the motion of liquids and gases on chemical reactions and the influence of physicochemical factors on the motion of liquids. Levich and his coworkers developed a theory of convective diffusion and heat transfer in turbulent liquid flow, a theory of the elementary act in liquid extraction and gas scrubbing, and methods of solving mass- and heat-transfer problems in a static or fluidised granular bed. The pioneering work on diffusion kinetics in the USSR was done by Frank-Kamenetskii, but Yu.S.Elovich and O.M.Todes also made contributions in this area.

M.F.Nagiev, Yu.G.Mamedaliev, and S.D.Mekhtiev (Academy of Sciences of the Azerbaidzhan SSR) investigated the kinetics of industrial systems, mainly with a view to developing improved methods of petroleum refining.

The volume of work on homogeneous catalytic reaction in our country is also very considerable, but relatively little research has been aimed specifically at the mechanism of homogeneous catalysis.

Thus, the Institute of Chemical Physics has developed, from its studies of the kinetics and mechanism of slow, liquid-phase alkene oxidation reactions, a method for the production of acetic acid, ethyl methyl ketone, and ethyl acetate by the oxidation of compressed butane, and also a promising method of preparation of alkene oxides by the simultaneous oxidation of alkenes and other organic compounds in the liquid phase.

E.A.Shilov (Academy of Sciences of the Ukrainian SSR) has made valuable contributions to the study of homogeneous catalytic reactions.

The problem of homogeneous catalytic synthetic reactions with organometallic complex catalysts is of intrinsic interest. These catalysts are widely used in the chemistry of high-molecular-weight compounds. We shall mention only the work at the Institute of Organoelemental Compounds, which demonstrated in principle the possibility of the fixation of atmospheric nitrogen by means of compounds of this type (M. E. Vol'pin), and similar work at the outstation of the Institute of Chemical Physics (E. A. Shilov).

ELECTROCHEMISTRY

The earliest electrochemical work in our country is associated with the names of M. V. Lomonosov, V. V. Petrov, F. F. Grotthus, B. S. Yakobi, E. Kh. Lents, A. S. Savel'ev, A. P. Sokolov, and others.

With the Soviet era, broad and comprehensive development began; this allowed Soviet electrochemistry to occupy one of the leading positions in world science.

The interest in electrochemical problems, and particularly in electrochemical kinetics, grew even stronger in the following years.

The work done in our country (initially, at the Academy of Sciences) on the theory of the electrical double layer, on the influence of adsorption on the kinetics of electrode processes, on the role of diffusion factors, on the theory of hydrogen overpotential, on the quantum-mechanical theory of electrode processes, on the electrochemical theory of corrosion and passivity, on the mechanism of metal electrodeposition, and on fused salt electrochemistry all played a major role in developing the theoretical foundations and the experimental methods of modern electrochemistry [22,23].

The establishments engaged on the solution of these problems include: the Institute of Electrochemistry of the Academy of Sciences of the USSR, the Institute of Physical Chemistry of the Academy of Sciences of the USSR, the Institute of Electrochemistry of the Urals Section of the Academy of Sciences of the USSR, the Institute of Physical and Organic Chemistry of the Academy of Sciences of the USSR (Kazan'), the Institute of Chemistry of the Academy of Sciences of the Lithuanian SSR, the Institutes of the Academy of Sciences of the Ukrainian SSR, the Karpov Physicochemical Institute, and many universities.

The most important electrochemical school in our country is the school of A. N. Frumkin, whose activities were associated at various times with the Karpov Physicochemical Institute, the Institute of Physical Chemistry of the Academy of Sciences of the USSR, and since 1958 with the Institute of Electrochemistry of the Academy of Sciences of the USSR [24].

Frumkin and his coworkers (B. N. Kabanov, R. Kh. Burshtein, N. A. Bakh, Ya. M. Kolotyrkin, M. A. Proskurnin, O. A. Esin, B. V. Ershler, V. I. Veselovskii, P. D. Lukovtsev, P. I. Dolin, Z. A. Iofa, V. S. Bagotskii, B. B. Damaskin, and others) started from the assumption that a close link exists between the mechanism of an electrochemical process on the one hand and the structure and electrochemical properties of metal surfaces and of the metal–solution interface on the other hand. Their theoretical and experimental work, for which new methods had to be developed, has added considerable depth to our understanding of the structure of these interfaces, and in particular they have allowed us for the first time to identify the correct value of the double layer capacitance and to correlate adsorption from solutions with the appearance of potential jumps at the electrode. They provided a solution for the so-called Volta problem (which had occupied electrochemists since the beginning of the previous century) regarding the relationship between the electromotive force of a galvanic cell and the contact potentials which appear when the metals are placed in contact in a vacuum.

The zero-charge potential was introduced into electrochemistry as a factor defining the adsorption properties and many electrochemical properties of metals, and various methods of measuring this potential were developed.

The work of the Soviet school of electrochemists has made possible some striking advances in our theoretical understanding of the structure of the electrical double layer. A paper by Frumkin published in 1919 gave a thermodynamic derivation and a test of the basic equation of electrocapillarity, by means of which the charge on the electrode and the adsorption of various components from the solution on the electrode surface can be calculated from measurements of surface tension. The electrocapillarity method was used to investigate the electrical double layer in non-aqueous solutions. Subsequently, electrocapillarity measurements and measurements of electrode capacity were widely used by Soviet electrochemists in studies of the electrical double layer on many liquid and solid metals.

The work of O. A. Esin, B. V. Ershler, and V. G. Levich contributed significantly to the development of double layer theory.

This school established the mechanism and the kinetics of some important electrode processes, such as hydrogen evolution, the evolution and the reduction of oxygen, and the reduction of chlorine in a number of anions and organic compounds; they showed that in many instances the rate of the overall process is determined by the rate of the electron transfer stage (from the metal surface to the reacting species).

Ershler and P. I. Dolin showed that the rates of fast electrochemical reactions can be measured by using alternating current: this was the first step towards the measurement of electrode processes under non-stationary conditions.

All this work played a major part in the creation of a new branch of chemical science—electrochemical kinetics—and provided a bridge linking electrochemistry to colloid chemistry, adsorption theory, catalysis theory, etc.

More recently, Levich developed the first physically sound theory of diffusion in moving liquids and of matter transport to the electrode surface, which enables the maximal current to be calculated under given conditions of mixing. On the basis of this theory, he proposed the rotating disc electrode as a tool for studying diffusion phenomena in electrochemical processes: this electrode is now widely used both in this country and abroad. Workers at the Institute of Electrochemistry of the Academy of Sciences and in the Department of Electrochemistry of Moscow State University developed a theory of the structure of the double layer on platinum group metals (A. N. Frumkin, N. A. Balashova, and O. A. Petrii), discovered a new form of discharge (which they termed barrierless discharge), and published the first experimental determination of an important constant—the adsorption energy of a hydrogen atom on a mercury electrode surface (L. I. Krishtalik).

Among the theoretical work on the electrochemistry of organic compounds we must mention also an extensive

series of investigations of electrolytic reduction reactions involving the participation of adsorbed organic molecules, carried out at the Institute of Electrochemistry of the Academy of Sciences (G. A. Tedoradze) and at the Institute of Organic Chemistry of the Academy of Sciences (S.G. Mairanovskii).

Theoretical electrochemistry provides the foundations for the solution of a number of problems of major importance to the national economy. A problem of the utmost importance is the realisation of fuel cells—devices in which the chemical energy of the fuel can be directly converted into electrical energy. Fuel cells are already used in astronautics: in the relatively near future we can expect to see them used in transport and in a number of specialised applications, and later perhaps in power generation. The pioneering work in this field in the Soviet Union was done by O.K. Davtyan of the Energetics Institute of the Academy of Sciences of the USSR. In recent years success was reported in studying the mechanism of processes taking place in fuel cells. Model systems have been analysed and a theory of porous electrodes was developed to allow their surface to be used efficiently (Institute of Electrochemistry of the Academy of Sciences, Karpov Institute, Odessa State University, Dnepropetrovsk Institute of Chemical Technology). The most satisfactory method (disc electrode with a ring) was developed for studying the electrolytic reduction of oxygen at the positive electrode of a fuel cell (Institute of Electrochemistry and Moscow State University). Progress is being made on the mechanism of electrolytic oxidation of organic compounds likely to be used as electrochemical fuels (Institute of Electrochemistry). A theory of the electronic conduction of solid electrolytes in equilibrium with a gas phase has been developed to describe the operation of fuel cells based on these electrolytes (Institute of Electrochemistry of the Urals Section of the Academy of Sciences of the USSR).

A great deal of interest attaches to the recently developed electrochemical transducers (memory cells, integrators, pressure and acceleration detectors, etc.) which effectively complement semiconductor devices in the low-frequency and the low-signal-power field. These devices are particularly suited for use in learning and self-organising systems. Various transducers have already been developed, including electrochemical transmitters capable of detecting mechanical vibrations with a sensitivity often orders of magnitude greater than that of existing systems, notwithstanding their much smaller size (P. D. Lukovtsev, Institute of Electrochemistry, and N.S. Lidorenko, All-Union Scientific Research Institute for Fuel Utilisation).

Research is in progress on advanced electrochemical methods of metal treatment: electrochemical machining, based on intensive anodic dissolution at high current densities, and electrochemical polishing. These methods are often more effective, faster, and cheaper than mechanical methods, particularly for very hard and refractory alloys {TsNIMS [Central Research Institute for Mechanical Construction? (Ed. of Translation)], Institute of Electrochemistry}. The mechanism of these processes has been investigated, and the role of kinetic and ohmic factors identified. The collaboration between industry and the Academy of Sciences produced excellent results in this instance.

Among the contributions of the institutes of the Academy of Sciences, mention must be made of the work of the Institute of Organic and Physical Chemistry on electrodeposition, anodic dissolution, and electropolishing of metals (G.S. Vozdvizhenskii) and of the work of the Institute of Physical Chemistry on the electrodeposition of metals.

The work of K.M. Gorbunova and P.D. Dankov on the mechanism of crystal growth and on nucleation processes during electrolysis was a pioneering effort. It was followed by numerous important investigations of the electrodeposition of alloys at the Institute of Physical Chemistry (K.M. Gorbunova and Yu. M. Polukarov), of the growth mechanism of dendrites during electrolysis, of the influence of adsorbed foreign materials on the electrodeposition of metals, and of the effect of temperature on the behaviour of electrodes with a slow exchange step (A.T. Vagramyan and coworkers).

At the Mendeleev Institute of Chemical Technology, the kinetics of electrode processes has been investigated over a wide range of temperatures (S.V. Gorbachev), the mechanism of electrochemical dimerisation has been examined in connection with the problem of electrolytic synthesis (M. Ya. Fioshin), new methods of electroplating have been developed, and their mechanism has been investigated (N.T. Kudryavtsev). More recently, the mode of action of levelling agents has been examined (S.S. Kruglikov).

Studies of electrochemical kinetics in fused salts are of great importance both from the practical and the theoretical point of view. The earliest work of this type was reported by S. V. Karpachev in the 1930's. O. A. Esin made systematic polarisation measurements in fused slags, M. V. Smirnov and S.I. Rempel' in halides. These researches showed that although the majority of chemical reactions are diffusion-controlled at high temperatures, slow discharge processes are also observed in some instances (for example, hydrogen evolution.

All the main data on the structure of the electrical double layer at the boundary between fused metals and electrolytes have also been established in our country (S.V. Karpachev, A.T. Stromberg, V.A. Kuznetsov, E.A. Ukshe).

Yu.K. Delimarskii and other Ukrainian electrochemists developed the polarography of fused salts and studied the specific features of diffusion-controlled kinetics in the same media. One important result of this work was to show that solid electrodes can be used for polarography, and also the application of polarography to the study of complex formation in melts.

Mention must be made also of the recently developed studies of the kinetics of electrodeposition from fused salts (K.M. Gorbunova of the Institute of Physical Chemistry, M.V. Smirnov of the Institute of Electrochemistry of the Urals Section of the Academy of Sciences, and others). In this work, which was primarily aimed at the electrolytic production of refractory metals, phenomena such as the dependence of the number of crystallisation centres upon the electrolysis parameters were first discovered and investigated in fused salts.

The study of corrosion processes is an aspect of electrochemistry of great practical importance. The basic studies of corrosion processes and of corrosion protection were started by V.A. Kistyakovskii at the Academy of Sciences; the work of N.A. Izgaryshev also contributed to the early development of corrosion science. The study of corrosion processes began to develop very rapidly as a result of the work of G.V. Akimov and his students (N.D. Tomashov, I.L. Rozenfel'd), who developed the theory of multi-electrode systems to predict the corrosion behaviour of each

constituent of a complex system, to investigate structural corrosion and the role of local cells, to explain the mechanism of corrosion in the presence of atmospheric oxygen, and to study the nature and protective properties of oxide films[24].

A.N. Frumkin, Yu.M. Kolotyrkin, Ya.V. Durdin, and others established the mechanism of corrosion of uniform metal surfaces, thus creating a bridge between corrosion theory and electrochemical kinetics.

As well as solving the above theoretical corrosion problems, the corrosion scientists of the Academy of Sciences contributed to the solution of many practical problems in the fields of atomic energy, aircraft and rocket design, shipbuilding, and the chemical and petroleum industry.

At the Institute of Physical Chemistry, the main centre of corrosion studies of the Academy of Sciences, many important investigations were carried out. Various coatings were tested, some of which have been adopted for the national network of pipelines, including the "Druzhba" oil pipeline. Electrochemical protection methods for underground and submarine equipment were developed and widely exploited. New gas pipelines were provided with protective devices. A new method of protection against stray currents, relying on the simultaneous use of protectors and germanium rectifiers, has been proposed and is being introduced into industrial practice. A new class of compounds has been synthesised (salts of amines and nitrobenzoic acids) with strongly corrosion-inhibiting properties towards both ferrous and non-ferrous metals. New methods of protection of components and complicated structures by volatile and contact inhibitors have been developed and handed over to industry. The scientific principle of corrosion resistant alloys based on titanium and zirconium and offering high-grade mechanical and anticorrosion properties have been proposed. The methods of protection of building structures developed at the Institute have been adopted and specified by the Department of State Construction.

A method of deposition of thin ferromagnetic films by chemical nickel plating has been worked out. The films produced in this way show a low coercive force and can be used for magnetic screening of complicated radio components. The basic features of the electrodeposition of alloys of refractory metals (titanium, tungsten, etc.) have been studied. The formulations and operating conditions proposed for electropolishing have been widely used in the finishing of heat-resistant alloys for aviation engines.

Valuable work in the field of protection against metal corrosion has been done also at the Karpov Institute. Thus, Kolotyrkin investigated the corrosion and electrochemical behaviour of a series of metals and alloys in aqueous media and pointed out the rules controlling their passivation. This work strengthened and stimulated the adsorption theory of passivity, whose foundations had been laid by B.V. Ershler and B.N. Kabanov.

Kolotyrkin's work on the mechanism of passivator action, which led to the formulation of the basic theory of the mode of action of oxidation and cathodic inhibitors, was applied to the solution of many problems of the corrosion stability of metals and alloys at high temperatures and pressure, and also in the presence of energetic radiations. At the present time Kolotyrkin is engaged on the practical exploitation of anodic protection of metals against corrosion.

Kolotyrkin also formulated the basic theory of pitting corrosion, which was confirmed by systematic studies of the dissolution of zirconium, iron, and iron alloys.

Recent work at the Department of Electrochemistry of Moscow State University (V.N. Korshunov) and at the Karpov Institute (Ya.M. Kolotyrkin, T.M. Florianovich) has shown that metal corrosion in aqueous solutions may occur not only by an electrochemical but also by a chemical mechanism, that is, without distinguishable anodic and cathodic processes. L.I. Antropov (Kiev Polytechnic Institute) has carried out a major series of investigations on the effect of the point of zero charge on the corrosion behaviour of metals and on the adsorption of corrosion inhibitors.

LIQUIDS. SOLUTIONS

Soviet scientists have always occupied a leading position in the study of solutions. Those who were already highly respected workers at the time of the October Revolution, such as M.S. Vrevskii, I.A. Kablukov, V.A. Kistyakovskii, and D.P. Konovalov, later gathered around themselves younger talent and thus laid the foundations of a number of Soviet schools of physical chemists, some of whose names are now widely known.

We shall mention first of all the work which had the greatest influence on the overall problem. Ya.I. Frenkel' was the first to attempt a systematic phenomenological theory of the liquid state on the basis of the nature of the motion of molecules in liquids. For a given molecule, this motion is determined by the molecular field generated by its surroundings and by its own kinetic energy, it follows a discontinuous path, and is characterised by a mean lifetime in temporary equilibrium positions. The basic ideas evolved by Frenkel' provided the foundations for the work of many authors.

N.N. Bogolyubov developed a general approach to the calculation of the thermodynamic properties of one-component and multicomponent systems from studies of the molecular distribution functions of groups of particles. A statistically consistent method of calculating the thermodynamic properties of strong electrolyte solutions, based on the correlation function and variational derivative method, is now widely used by Soviet and foreign theoreticians to solve stochastic problems. The method has been developed in papers by I.Z. Fisher, who examined in particular its application to problems of liquid structure. V.I. Danilov and his school carried out some fundamental work on an experimental method for determining the structure of pure liquids and solutions.

The most interesting and general result obtained by this method was to demonstrate the presence in liquids of short-range order as found in crystals. In a series of theoretical and experimental investigations, M.I. Shakhparonov developed a method of studying the microstructure of liquids and solutions by radiofrequency, optical, and acoustic measurements. His main result was to show that the positions of molecules fluctuate, causing the local physical properties of liquids to differ from their macroscopic values. A.V. Storonkin established by a formal thermodynamic analysis the possible types of phase equilibrium curves in heterogeneous multicomponent systems, including the vapour phase.

A series of papers by I.R. Krichevskii on phase transformations in solutions of non-electrolytes under high pressure made an important contribution to a correct understanding of the relationship between particle–particle interactions and the thermodynamic properties.

Many important results were obtained in the field of electrolyte solution theory. V.K.Semenchenko first put forward the view that ion pair formation affects the behaviour of electrolyte solutions, and gave a physical model of the phenomenon and an approximate mathematical treatment. A similar hypothesis was independently put forward, somewhat later, by Bjerrum, but improvements to his mathematical treatment are still being proposed. S.V.Tyablik and V.V.Tolmachev showed, by Bogolyubov's correlation function method, that the Semenchenko–Bjerrum correction for ionic association is obtained automatically when the free energy of an electrolyte solution is calculated by a systematic statistical approach. V.G. Levich and V.A.Kir'yanov used Bogolyubov's method to derive the most general expression for the free energy of an electrolyte solution, in which the Coulombic potential at small distances is replaced by an arbitrary potential. The expression obtained can, according to the form of the potential chosen, describe purely Coulombic interaction or alternatively it can describe the Brønsted–Guggenheim "specific" interaction of ions with a non-Coulombic short-range interaction. Yu.M.Kossler discussed the physical principles underlying the non-Coulombic components of the potential. G.I.Mikulin proposed a numerical method of solving the Poisson–Boltzmann equation in which account is taken of the variation of the dielectric constant with distance from the centre of the ion. This method is strictly accurate, unlike some even more recent work by various foreign authors.

The thermodynamics of ion solvation has made significant progress through the efforts of a number of scientists. V.A.Pleskov put forward the idea that the solvation energies in different solvents must tend towards a common value as the radius of the ion increases. Hence, by choosing an electrode reversible to the ion for which these energies are practically equal it is possible to compare the chemical solvation energies of various ions (which are not experimentally measurable). His researches with a series of non-aqueous solvents showed that caesium or rubidium can be used as the electrode. A.F.Kapustinskii had some interesting views on the difference between the true radii of ions in aqueous solutions and their crystal-chemical radii. His corrections (±0.28 Å) were applied by N.A.Izmailov to resolve the total hydration energy into its components for ions. Unlike others who made similar attempts, Izmailov suggested extrapolating the sums and differences of the solvation energies of a given ion with a number of other ions of increasing radius to infinite ionic radius. This method is independent of any hypothesis on the structure of solutions. K.B.Yatsimirskii made valuable studies of specific aspects of the energy of formation of ions, of proton affinity, and of ion hydration.

Problems of the structure of electrolyte solutions are attracting a great deal of attention at the moment in the USSR. This work is largely associated with the name of Kapustinskii, who used Fowler and Bernal's tetrahedral model of the water structure in his study of the heat capacity of ions in aqueous solutions and showed that the structure of the solvent must be considered when discussing the thermal motion of ions. O.Ya Samoilov perfected the tetrahedral model by allowing for partial filling of the holes in the ice-like skeleton by water molecules set free by its thermal motion and, by using the ideas of Frenkel', he constructed a consistent model of the structure of water solutions and of the hydration of ions. His concept of positive and negative hydration proved very fruitful in allowing structural and thermodynamic approaches to be unified (for example, the distribution of an electrolyte between water and an immiscible solvent). A series of contributions by K P.Mishchenko and coworkers used the thermodynamic relative partial molal properties to characterise the structure of electrolyte solutions. The specific intersection of composition–property isotherms led Mishchenko to introduce the concept of a real solvation boundary, which reflects the structural and energetic aspects of the process.

A large group of papers by V.A.Plotnikov and his students, who studied the physicochemical and electrochemical properties of a wide range of non-aqueous solutions, forms a slightly isolated topic. Their main contribution was to demonstrate the relationship between these properties and complex formation, and a vast fund of factual data on the cathodic deposition of metals.

Studies of solutions under extreme conditions (temperatures up to 400°C) were undertaken on a broad scale for the first time in the USSR by I.S.Galinker. These studies produced interesting experimental results, relevant to an understanding of the structural properties of water.

The glass electrode, whose theory was developed in detail by B.P.Nikol'skii, plays an important part in measurements of the electrode potentials of hydrogen and alkali metal ions, which are needed in thermodynamic calculations Techniques for the preparation of glass electrodes suited to different types of measurement were also developed in Nikol'skii's laboratory.

The theory of acids and based was considerably developed by the work of A.I Shatenshtein, N A Izmailov, and M.I. Usanovich. Shatenshtein and Usanovich broadened and generalised the concept of acids and bases so as to include acid–base interactions not involving ionisation. This allowed them to include reactions not considered in Brønsted's previous scheme, to introduce the concept of acid-like aprotic substances and to show that the acidic (or basic) properties of a substance depend to a considerable extent on the protonophilic (or acidic) properties of its reaction partner. Izmailov discovered and investigated the influence of solvent on the relative strength of acids and bases, which results from interactions with the solvent (solvation), and originated unified studies of acidity.

RADIATION CHEMISTRY

Radiation chemistry became a discipline in its own right during the last two decades, coinciding with the practical application of atomic energy.

Our scientists have contributed very significantly to the creation of the theoretical foundations of radiation chemistry by their work on ion–molecule reactions, energy transfer during radiolysis, the radiolysis of aqueous and of organic systems, the formation and transformations of free radicals and ions in irradiated solids, radiation-induced polymerisation in the solid phase, etc.[26-28]

It may now be claimed that radiation chemistry in the Soviet Union is on a level with world radiation chemistry.

The institutes of the Academy of Sciences (Institute of Chemical Physics, Institute of Electrochemistry, Institute of Physical Chemistry, Institute of Petrochemical Synthesis), the Karpov Institute, and the Chemistry Faculty of Moscow State University have all been involved in the development of radiation chemistry.

Studies of the radiolysis of inorganic and organic systems occupy an important place among Soviet researches in this field.

The work on radiation-chemical changes in solid and in liquid organic compounds was done mainly by N. A. Bakh, Kh. S. Bagdasar'yan, M. A. Proskurnin, N. Ya. Buben, L. S. Polak, and V. L. Tal'roze. These workers clarified the role of ions, free thermalised electrons, and free radicals in radiolysis processes in condensed media. The radiolysis products were identified and investigated, and many radiation-chemical changes in organic compounds were characterised quantitatively.

Much of the work on free radicals in condensed phases was done by the ESR method, whose development owes a great deal to Soviet workers. The method allows the detection, identification, and quantitative estimation of free radicals formed as intermediate radiolysis products. This work was done by N. A. Bakh, N. Ya. Buben, V. V. Voevodskii, L. S. Polak, S. Ya. Pshezhetskii, and others.

Studies of radiation-induced oxidation began in 1949 in the Soviet Union, mainly under the direction of Bakh. The first studies were aimed at the determination and identification of the oxidation products of liquid hydrocarbons of different structures. It was shown that the yield depends on the nature of the hydrocarbon and on the irradiation conditions, whereas the mechanism of the processes involved depends on the temperature.

The radiolysis of water and aqueous solutions is the most widely investigated topic in radiation chemistry, because of the extensive use of water in atomic technology and reactor design. The work of the Soviet scientists P. I. Dolin, V. I. Veselovskii, B. V. Ershler, M. A. Proskurnin, and others, in the period 1946–1955, led to the development of the free-radical mechanism of the radiolysis of water independently of foreign workers, who reached similar conclusions.

The sensitising effect of solid surfaces on radiation-chemical processes in liquid systems was discovered by the Soviet scientists L. V. Pisarzhevskii and V. I. Veselovskii. This work is now continuing at the Institute of Petrochemical Synthesis, at the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, and elsewhere; the effect of irradiation on catalytic processes in general is also being investigated (Karpov Physicochemical Institute, Institute of Physical Chemistry, and Institute of Chemical Physics of the Academy of Sciences of the USSR, etc.).

The first papers on the acceleration of topochemical processes by previous treatment by ionising radiation appeared in 1955–1956. In the following years a large number of investigations in this field, carried out under the direction of S. Z. Roginskii, G. M. Zhabrova, and V. V. Boldyreva, were reported.

Systematic studies of the radiation chemistry of polymers were pursued mainly at the Karpov Physicochemical Institute and at the Institute of Physical Chemistry of the Academy of Sciences of the USSR. Initially, this work was aimed at solving problems arising in the use of polymeric materials in the handling and application of radioactive materials. The main effort was directed towards the radiation-induced degradation of polymeric materials and changes in their physico-mechanical properties under the influence of radiation. However, the essential experimental facts about radiation-chemical changes in polymeric systems were established at an early stage and the first views on the nature of the processes involved were put forward.

Subsequently, the effort on various aspects of the radiation chemistry of polymers was extended by the numerous research institutions whose primary interest was to investigate the possible use of radiation-chemical processes for the controlled modification of polymeric materials, principally in the direction of radiation-induced vulcanisation.

V. A. Kargin and V. L. Karpov proposed the use of ionising radiations for vulcanising polyethylene, which could not be vulcanised in any other way. S. S. Medvedev and A. D. Abkin made a detailed study of the radiation polymerisation of various monomers in the liquid and the gas phase. V. I. Gol'danskii's method of cross-linking different monomers by the localised action of thermal neutrons has proved very valuable.

The radiation method offers very wide scope for including polymerisation reactions in the solid phase. A very promising technique has been developed at the Institute of Electrochemistry of the Academy of Sciences of the USSR and at the Institute of Physical Chemistry of the Academy of Sciences of the USSR for gas-phase radiation-induced graft copolymerisation, which allows combined inorganic–organic materials to be prepared as well as sheathed filaments and two-layer films combining the properties of the initial (inner) layer with those of the outer layer formed by the grafted polymer.

A method of improving wood cellulose by impregnating it with various monomers and polymerising them with gamma radiation, proposed in 1958 in the Soviet Union, has achieved great technological importance.

A number of radiation-chemical processes are now fully developed and have reached the stage of pilot-plant production: they include the cross-linking of thermally stabilised polyethylene, the telomerisation of ethylene, the oxidation of paraffins, the sulphochlorination of Synthin [a fuel (Ed. of Translation)], and the production of special-purpose rubbers.

PHYSICAL CHEMISTRY OF SURFACE PHENOMENA. ADSORPTION. CHROMATOGRAPHY

The variation of the properties of colloidal systems with the degree of subdivision of the disperse phase and the stability of these systems were investigated by A. V. Dumanskii (Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR) and by N. P. Peskov. Their conclusions have been widely applied in Soviet soil science as well as in the control side of the food industry.

The rapid growth of the high-polymers industry (plastics, elastomers, viscose, synthetic fibres) has stimulated the development of research on lyophilic colloids, a term which was then applied to polymers in colloidal chemistry. The work of A. V. Dumanskii, S. M. Lipatov, V. A. Kargin, and B. A. Dogadkin[29] is noteworthy in this area. This topic subsequently merged into the developing field of polymer chemistry.

Research on the physical chemistry of surface phenomena is centred at the moment on the Institute of Physical Chemistry, the Karpov Institute, Moscow State University, and some associated institutes.

By 1935, a Disperse Systems Division had been set up at the Institute of Colloidal and Electrochemistry under the leadership of P. A. Rebinder. He and his coworkers (A. B. Taubman, V. I. Likhtman, E. D. Shchukin, and others) developed a number of aspects of modern colloid chemistry, and they also created a new interdisciplinary area of chemical science—the physicochemical mechanics of disperse structures, solids, and technical materials. The features and mechanisms of the formation and development of disperse structures, leading to the synthesis of fine-grained, strong, and durable solids and technical materials, were investigated, as well as the deformation and disintegration of solids of various compositions and degrees of dispersion (from fully dense and strong bodies to finely porous solids of varying and occasionally high porosity[30]).

This work led to many essentially new results of great scientific and economic importance. We note first of all the effect producing easy deformation of solids and decreased strength under the influence of an active medium or low amounts of adsorbed substances (the so-called Rebinder effect). The discovery of this effect led to the development of methods now used under industrial conditions for ultrafine grinding and to the softening solution method for raising the efficiency of drilling in hard rock. New high-efficiency lubricating coolants for the working and cutting of metals were proposed. Scientific foundations were developed for optimising the manufacture of precast concrete and reinforced concrete, and also sand concrete without coarse fillers.

Rebinder developed new physicochemical ideas on the three-dimensional structures arising with disperse and colloidal systems. He established the rheological characteristics of structures of various types, the rules governing their structural and mechanical properties, and methods of controlling these properties. The effect of the interfacial surface energy on the formation of disperse systems—whether involving dispersion or condensation (formation of new disperse phases)—was investigated theoretically and experimentally, including the conditions for spontaneous dispersion. The detailed study of the properties of soap-like surface-active agents (semicolloids of both the ionogenic and the non-ionogenic type) led to the scientific formulation of many valuable applications of surface-active materials in many areas of the national economy (detergents, wetting agents, flotation agents, stabilising and dispersing agents, de-emulsifiers, lubricating coolants, and lubricants, etc.).

Another new development begun in 1935 at the Institute for Colloidal and Electrochemistry under the direction of B. V. Deryagin was the study of surface phenomena with special emphasis on the action of surface forces close to the interface. The extensive investigations made by Deryagin and his coworkers played a fundamental part in the development of the science of surface forces and of their role in the kinetics of physicochemical processes in heterogeneous systems and in colloidal chemistry.

Having discovered and investigated one of the fundamental thermodynamic characteristics of thin layers—the disjoining pressure—Deryagin developed a quantitative theory of the stability of lyophobic colloids. The methods of calculation which he first developed for the repulsion forces arising from the overlapping of ionic atmospheres provided a basis for the currently accepted theory of the stability of lyophobic colloids.

The same laboratory developed a theory of the flotation of mineral particles whose conclusions have been applied practically. Allowance for ion diffusion led to refinements in the modern theory of electrokinetic phenomena, including electrophoresis. The chemical and morphological characteristics of individual soil particles were correlated with the behaviour of soils during application and removal of loads, slip, and filtration. From studies of the physical chemistry of thin water films, a theory was developed to explain the mechanism of migration of moisture and petroleum in porous media.

Deryagin made the first direct measurements of molecular attraction as a function of distance between different solids. His results were subsequently repeated by workers in England and in the Netherlands, and confirmed the modern theory of molecular forces.

Various methods worked out by Deryagin led to the conclusion that the surface of a lyophilic solid can modify the structure and properties of the adjacent layers of liquid to a depth of at least tens of molecular diameters. More recently, previously unknown properties of bulk liquids were discovered as a result of this work.

Researches in the field of aerosols have had far-reaching practical results; in particular, new methods of dispersion and precipitation of clouds and fog have been developed, and very efficient and economical condensation filters for the purification of air in mines have been designed.

At the Institute of Physical Chemistry, A. A. Trapeznikov developed new concepts and exploited methods of investigation and apparatus for the rheology of structured systems, and for studying the combined effects of deformation-resisting properties and relaxation in the pre-stationary stage; he also proposed generalised concepts of fluidity limits. His contribution included studies of the mechanical properties of monolayers and soap films formed by insoluble and by soluble surface-active materials.

A laboratory for colloid chemistry was set up by A. P. Rabinovich at the Karpov Institute in 1924. The relationship between ion adsorption processes and the stability of hydrophobic colloids was studied by electrochemical methods, and the important role of ion exchange at the surface of colloidal particles was recognised. Rabinovich was also responsible for the adsorption theory of development, which now forms the basis of photographic science.

Subsequent work in this laboratory, by V. A. Kargin and Z. Ya. Berestneva, demonstrated the important role of chemical phenomena in the behaviour of colloidal systems. It was found that practically all colloidal solutions contain significant amounts of stabilising electrolytes which react chemically with coagulants, and that dealing exclusively with the physical phenomena which take place during coagulation is too coarse an approximation. Chemical reactions between substances in the colloidal state were found to proceed in true solution by gradual dissolution of the particles.

More recently, the application of electron microscopy has enabled the mechanism of formation of colloidal particles to be identified. The first stage was shown to be the formation of large, usually spherical, amorphous particles which then recrystallise and break down into the very fine crystalline particles typical of colloidal solutions.

I. V. Petryanov-Sokolov of the Karpov Institute carried out comprehensive studies in the physical chemistry of aerosol systems. His work and that of his colleagues on the physicochemical properties of aerosols, extending over many years, proved to be a fundamental contribution to science. They developed quantitative methods for the

experimental study of the degree of dispersion of aerosols which are now widely applied, and which have led to the solution of a number of problems concerning the electrical properties of aerosols.

Petryanov-Sokolov made a detailed study of the stability of undischarged aerosols. A series of researches was devoted to the previously unrecognised problem of the behaviour of the disperse phase of an aerosol when the particles are deposited on the fibres of a filter. This work led to the development of novel, important, and widely used processes.

A. N. Fuks and N. N. Tunitskii did some important work at the Institute on the formation and coagulation of aerosols.

Ya. I. Kogan made some important contributions to the development of experimental techniques for studying aerosols, and of methods, devices, and apparatus for testing under industrial conditions the efficiency of a wide range of aerosol filters.

From their studies of the optical properties of aerosols, Kogan and his coworkers designed highly sensitive nephelometers which are now extensively used. The application of his aerosol flocculation method led Kogan to the discovery of molecular condensation nuclei and to the development of unusually sensitive methods of measuring gaseous impurities in air. This work suggested that molecular counters for gaseous impurities can be designed.

A. M. Amelin made an extensive investigation of all instances of formation of supersaturated vapour. He derived numerical formulae for predicting fog formation, for determining its concentration, and for developing fog prevention measures. He put forward a general theory of the formation of aerosols by condensation which is widely used to solve a variety of practical problems.

A Sorption Processes Laboratory (later, Section), led by M. M. Dubinin, was created in 1946 at the Institute of Physical Chemistry of the Academy of Sciences of the USSR. Its main scientific objective was to formulate and refine the theory of the physical adsorption of gases on porous solids. The activities of this laboratory maintained the continuity and the scientific traditions of the school of N. A. Shilov, one of the pioneers of adsorption studies in our country [31].

Extensive experimental and theoretical studies led to a rational classification of porosity which is at the same time a classification of the sorption processes. A quantitative theory of adsorption was developed for the so-called microporous adsorbents (active carbons, zeolites, etc.). This is the theory of volume filling, which permits calculation (from a limited amount of experimental data) of the parameters of the adsorption equilibrium with a precision beyond the scope of alternative modern theories of physical adsorption. In later work the theory was refined and generalised.

Significant results were obtained in the relatively unexplored but practically important field of the adsorption of mixtures of gases.

In addition to studies of adsorption equilibrium, the Section produced valuable results on adsorption kinetics which led to the solution of important problems in sorption technology. Mention must also be made of the important organising and coordinating role played by the Section in the general stream of scientific and technological research on sorption processes in the USSR. This role was recently formally recognised by the creation of the Scientific Committee on Adsorbents.

The Surface Chemistry Laboratory of the same Institute (A. V. Kiselev) has devoted its main effort to a comprehensive study of the chemistry of adsorbent surfaces and the nature of adsorption interactions. The basic adsorption and gas-chromatographic thermodynamic characteristics for various molecules, including hydrocarbons, have been calculated by the methods of statistical mechanics. Heats of adsorption and heat capacities have been measured in new, highly sensitive calorimeters for a number of important systems. The adsorption energy has been directly correlated with the structure of the adsorbed molecules (including macromolecules).

Work in the field of chromatographic analysis began to develop on a wide front in the USSR in 1946–1949, creating the need for a central institution which would coordinate and unify these investigations. A Chromatography Laboratory was created in 1949 at the Institute of Physical Chemistry of the Academy of Sciences of the USSR under K. V. Chmutov, and in 1950 the Scientific Committee on Chromatography was created. The Laboratory has been responsible for some major developments on theoretical and applied aspects of chromatography, including: the laws governing the statics, kinetics, and dynamics of the chromatographic process, the development and theoretical formulation of methods for separating the rare-earth elements, complex formation in chromatography, the radiation stability of ion-exchange materials, the development of new chromatographic methods (the adsorption–complexing method, the distribution chromatography of inorganic substances), the intensification of chromatographic processes (high temperatures and pressures), theoretical models of chromatographic processes, and the development of the most recent automatic apparatus for chromatography. Much of this work has great practical importance and has influenced industrial practice.

The work of A. A. Zhukhovitskii has contributed significantly to the development of a number of scientific topics: the thermodynamics of surface phenomena, the dynamics of adsorption processes, the theory of chromatography, and new variants of chromatographic analysis. Zhukhovitskii developed the theory of adsorption of mixed vapours and the theory of adsorption from solutions. He also made notable contributions to the theoretical foundations of gas and gas–liquid chromatography, and proposed new methods of chromatographic analysis.

The work on the theory of chromatography by N. N. Tunitskii (Karpov Institute) showed that the diffuseness of chromatographic bands arises from fluctuations in the lifetime of particles in the sorbed state. He developed new calculation methods for sorption separation processes which are relevant to the intensive purification of materials. Tunitskii has proposed a theory of the rate of ion exchange with allowance for the mobility of the ions taking part.

G. V. Samsonov (Institute of High-Molecular Compounds of the Academy of Sciences of the USSR) developed a theory of ion exchange on swelling resins which permits a rational choice of sorbent for the removal of some organic ions from complex mixtures. He synthesised carboxylic acid resins having an enhanced selectivity towards certain organic ions (streptomycin, colimycin). His work in the field of sorption is closely associated with the solution of practical problems in the development of technological methods of separation and purification.

In addition to the wide application of existing procedures and apparatus for gas chromatography, many institutions have contributed to the further development of chromatographic practice. The result of this work was a considerable increase in the sensitivity, generality, precision, and reliability of chromatographic methods. The Instrument Design Bureau of the Institute of Petrochemical Synthesis and that of the Institute of Organic Chemistry have played a major role in the development and practical exploitation of gas chromatography apparatus.

THERMODYNAMICS

Advances having major practical importance have been made in the Soviet Union in the study of the thermodynamic properties of special groups of materials used in modern technology (new fuels, semiconductor materials, rare metals, strong alloys, heat-resisting coatings, hard alloys, etc.).

Ya. I. Gerasimov is the leader of a major centre of thermodynamic research in our country—the Physical Chemistry Department of Moscow State University.

The scientific activities of Gerasimov and his coworkers are mainly aimed at the chemical thermodynamics of non-ferrous metallurgy, the thermodynamics of heat-resistant alloys, metal oxides, and semiconducting compounds. They successfully developed many new methods of measurement and investigation of thermodynamic quantities at high temperatures: this work has had a considerable impact on highly energetic systems and other areas of modern technology.

In the same Department, S. M. Skuratov of the Luginin Thermochemistry Laboratory is making high-precision measurements of the heats of combustion of organic compounds. The laboratory has developed a number of new methods.

The work of M. Kh. Karapet'yants in the field of thermodynamics, carried out at the Mendeleev Moscow Chemical Technology Institute, has gained wide recognition. He leads a new scientific project, involving the development and application of a group of methods, which he had originally suggested, of comparative calculation of the physicochemical properties of various substances and process parameters. These methods make possible the calculation of many physical and physicochemical constants from a limited number of experimental data (reference points). Particularly successful was the application by Karapet'yants of his comparative calculation method to evaluating the properties of homologous series of organic compounds (petrochemical calculations), isotope effects, the properties of complex compounds, the physical and physicochemical properties of semiconductors, silicate glasses, etc.

I. R. Krichevskii (State Institute for the Nitrogen Industry) discovered the new phenomenon of limited miscibility of gas phases and made a quantitative study of it in a number of systems. Equally noteworthy is a series of investigations under his direction of the solubility of gases in liquids under high pressures. Having developed accurate methods of investigation in the difficult high-pressure area up to tens of thousands of atmospheres, Krichevskii and his coworkers made a series of technologically important measurements. They also contributed to the development of the thermodynamics of dilute solutions and provided data for the development of the theory of intermolecular forces.

The problem of chemical equilibrium in complex mixtures at high temperatures is of importance in many fields of technology. We should note the experimental studies of equilibria in the thermal and catalytic cracking of hydrocarbons (A. V. Frost, A. A. Vvedenskii, and others), and the development of methods for thermodynamic calculations of combustion and explosion processes (Ya. B. Zel'dovich, A. N. Gurvich, Yu. M. Shaulov.

In the same general area, we note the work on the systematic statistical calculation of thermodynamic quantities for gases at high temperatures (A. V. Frost, I. N. Godnev, and a group of workers at the Institute of Fossil Fuels and the State Institute for Applied Chemistry).

Among the foremost theoretical investigations, mention must be made of the interesting work on second-order phase transformations (L. D. Landau, V. K. Semenchenko). A. V. Storonkin did some interesting work on solution–vapour equilibria in complex multicomponent systems. D. S. Korzhinskii evolved the theory of heterogeneous equilibria in multi-phase, multicomponent open systems, applicable to geological processes.

Many workers have investigated the thermodynamic functions of specific inorganic compounds, groups of compounds, solutions, and alloys, both in theoretical generalisations and in practical problems (mainly in the field of metallurgy). They include E. V. Britske (Scientific Institute of Fertilisers, Insecticides, and Fungicides), A. F. Kapustinskii, V. A. Sokolov, and N. K. Voskresenskaya (Institute of General and Inorganic Chemistry), A. I. Vol'skii (Mineral Institute for Non-Ferrous Metals and Gold), Ya. I. Gerasimov (Moscow State University), A. A. Zhukhovitskii (Institute of Steel), V. A. Kireev (Karpov Institute of Physical Chemistry), G. V. Kurdyumov (Central Scientific Research Institute for Ferrous Metallurgy), K. P. Mishchenko (Leningrad Chemical Technology Institute), M. M. Popov, K. G. Khomyakov, A. V. Rakovskii, S. M Skuratov, An. N. Nesmeyanov (Moscow State University), A. M. Samarin, N. V. Ageev, I. I. Kornilov (Institute of Metallurgy), and S. A. Shchukarev (Leningrad State University).

PHYSICOCHEMICAL ANALYSIS

Closely related to the thermodynamic investigations are the studies in the field of physicochemical analysis, which was created and widely developed in our country by the efforts of N. S. Kurnakov and his school (N. V. Ageev, V. Ya. Anosov, A. G. Grigor'ev, N. N. Efremov, S. F. Zhemchuzhnyi, V. A. Nemilov, S. A. Pogodin, N. I. Stepanov, G. G. Urazov, I. N. Lepeshkov, and others).

The work of Kurnakov's school has established the general principles of physicochemical analysis, led to new experimental methods, and accumulated and unified a vast amount of experimental information on systems consisting of the most varied components such as metals, oxides, sulphides, salts, organic compounds, etc.

From studies of these equilibrium diagrams, accurate conclusions have been made on the nature of the interactions between the components in the systems and on the nature and stability boundaries of the resulting phases (whether individual compounds or solid or liquid solutions).

The concept of singular points in chemical diagrams, introduced by Kurnakov, has made possible accurate discrimination of the chemical individuality of substances, and

has clarified the distinction between daltonides and berthollides, azeotropes, eutectics, cryohydrates, etc.

We cannot overemphasise the importance of the work of Kurnakov and his students in rationalising pyrometallurgical processes, preparing a large number of important alloys, and exploiting the mineral (particularly salt) resources of our country.

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THE TRANSFORMATION OF HYDROCARBONS WITH MEDIUM-SIZED RINGS IN THE PRESENCE OF PLATINUM CATALYSTS

B.A.Kazanskii, E.S.Balenkova, and S.I.Khromov

The chemistry of cyclic compounds with rings of medium dimensions, containing 8–12 carbon atoms in the molecule, has developed considerably in recent years. The interest in these compounds results from the important part which they played in theoretical organic chemistry, due to a number of unique features characteristic of this class of compound. These features include the unique geometric shape of the molecule and the consequent possibility of interaction between atoms of the same molecule, not directly joined to one another. This interaction in medium-sized rings may take place through the ring (transannular interaction) and may be produced between hydrogen atoms attached to neighbouring carbon atoms (vicinal interaction). Both of these factors lead to an increased energy content in medium-sized rings; this has been called "non-classical" conformational strain and is responsible for a number of characteristic features in the chemical and physical properties.

Transannular reactions not only are characteristic of functional derivatives of medium-sized rings but also take place in the catalytic transformation of hydrocarbons with rings of medium dimensions over hydrogenation–dehydrogenation catalysts. In 1955, Prelog and coworkers [1] observed for the first time the transformation of hydrocarbons containing 9–18 carbon atoms in the ring, over a palladium catalyst at 400°C. Depending on the number of

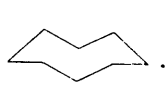
carbon atoms in the ring, removal of hydrogen gave various polycyclic, aromatic, and pseudo-aromatic hydrocarbons (indene, azulene, naphthalene, phenanthrene, etc. up to triphenylene). The hydrocarbons studied were divided into four groups, according to the nature of the transformations and the number of carbon atoms in the original ring:

(I) $C_5 + 4n$ C_9H_{18}; $C_{13}H_{26}$; $C_{17}H_{34}$
(II) $C_6 + 4n$ $C_{10}H_{20}$; $C_{14}H_{28}$; $C_{18}H_{36}$
(III) $C_7 + 4n$ $C_{11}H_{22}$; $C_{15}H_{30}$
(IV) $C_8 + 4n$ $C_{12}H_{24}$; $C_{16}H_{32}$

Hydrocarbons of group (I) are transformed into condensed systems with five-membered rings (for example, cyclononane forms indene). Of the hydrocarbons in group (II), cyclodecane gives azulene and naphthalene, and the others are converted into condensed compounds containing six-membered rings. Hydrocarbons of groups (III) and (IV) are converted into more complex condensed systems. For example, acenaphthene and acenaphthylene were found in the catalysate from cyclododecane.

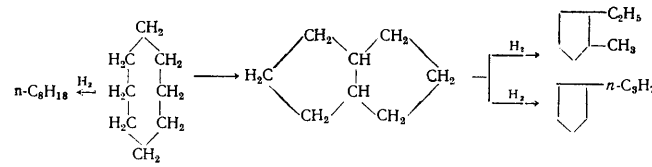
Prelog found only aromatic hydrocarbons in the reaction products. There is no doubt that by carrying out the reaction under different conditions, it is possible to find among them both primary and intermediate transformation products. The first stage of transannular dehydrocyclisation in alicyclic hydrocarbons with a medium-sized ring is probably C_5- or C_6-dehydrocyclisation[2] inside the ring. In this instance it would be expected that platinised carbon, which is a more specific dehydrocyclisation catalyst than palladised carbon, would be a more suitable catalyst for such transformations and that by carrying out the reaction at temperatures lower than those used in Prelog's work it would be possible to trap the products of the first stage of the transannular dehydrocyclisation, namely, such bicyclic hydrocarbons as hydrindane, decalin, perhydroazulene, etc.

As early as 1930, Zelinskii and Freiman[3] studied the behaviour of cyclo-octane in the presence of platinised carbon at 300°C and suggested that it is converted into bicyclo[3,3,0]octane (pentalane) and methylcycloheptane. From the modern viewpoint, the suggestion that pentalane is formed from cyclo-octane under these conditions is quite well-founded. In actual fact, according to modern conformational theories, cyclo-octane has the shape of a crown[4], in which four quasi-axial hydrogen atoms lie above the central plane of the eight-membered ring, and four lie below it: the atoms of each group of four are moved closer to one another towards the centre of the molecule; this on the one hand creates additional internal conformational strain and on the other hand facilitates the removal of the 1,5 hydrogen atoms when cyclo-octane is adsorbed on a catalyst surface at elevated temperature, as a result of which a transannular 1,5 C–C bond may be produced, with the formation of pentalane



In 1960 it was shown that on the surface of platinised carbon at 310°C cyclo-octane is almost completely converted into *cis*-pentalane, which then undergoes hydrogenolysis[5]. On a specially selected catalyst the yield of *cis*-pentalane can be increased to 70%.[6]

The reaction scheme is:



A small quantity of n-octane was found in the products of the transformation of cyclo-octane, so that the eight-membered ring undergoes direct hydrogenolysis, albeit to a very slight extent.

It might be assumed that the conformational characteristics of other multi-unit hydrocarbons would also play an important part in their transformations. Here, however, it must be borne in mind that the conditions of the reaction—elevated temperature and the presence of a catalyst—may lead to certain conformational changes in these cyclanes and the appearance of reaction products which do not come from their most stable conformations.

In 1960 an X-ray diffraction study was made of the structures of nine-, ten-, and twelve-membered rings[7-11]. The X-ray diffraction data were used to calculate the C–C–C valency angles, the torsion angles, and the length of the C–C bonds; this made it possible to obtain a picture of the most stable conformations of these rings and the position of the hydrogen atoms in the rings. It was found that the carbon framework of the cyclononane molecule is completely asymmetric, so that all 18 hydrogen atoms in it are non-equivalent. For practical purposes, however, Dunitz and Prelog[12] proposed their division into two groups: six intra-annular hydrogen atoms, directed into the ring, and twelve extra-annular Each of the six intra-annular hydrogen atoms approaches two others in space so that the shortest distance between them is about 1.8 Å (Fig. 1). This close positioning of the intra-annular hydrogen atoms facilitates their removal when the hydrocarbon molecule is adsorbed on a catalyst surface.

The ability of platinised carbon to catalyst the reactions of C_5- and C_6-dehydrocyclisation with the formation of five- and six-membered cyclanes and also condensed hydrocarbons with five- and six-membered rings suggests that when cyclononane is adsorbed on a catalyst surface, removal of the intra-annular hydrogen atoms on the first and fifth or third and eighth carbon atoms will take place readily, leading to the formation of hydrindane as chief reaction product.

In actual fact, the chief primary product of the transformations of cyclononane on platinised carbon at 300°C is

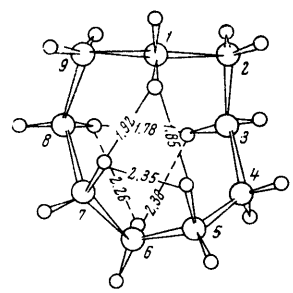
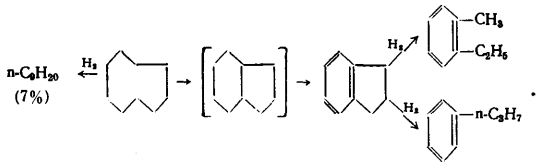


Fig. 1. Conformation of cyclononane.

hydrindane, which under the conditions of the experiment is immediately converted into indane. Hydrogenolysis of the five-membered ring in indane gives *o*-ethyltoluene and n-propylbenzene. For cyclononane a greater part is played by the second direction of the reaction—direct hydrogenolysis of the ring. The yield of n-nonane amounts to 7%.[13]

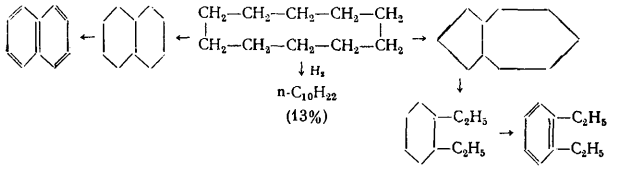
The cyclononane reacted according to the scheme:



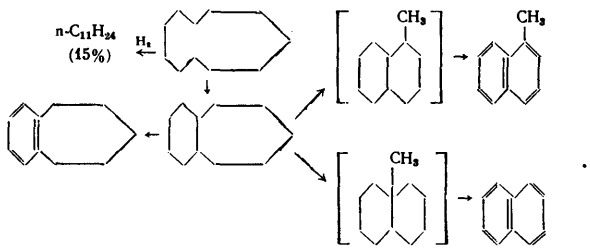
The cyclodecane molecule (Fig. 2) also has six intra-annular hydrogen atoms directed into the ring, and in this sense the geometries of the nine- and ten-membered rings show considerable similarity. Among the intra-annular hydrogen atoms, two pairs of atoms are moved together in the 1,5 position, and their removal under the reaction conditions should lead to the formation of decahydroazulene.

The products of the catalytic transformations of cyclodecane consisted of *cis*-decahydroazulene, 1,2-diethylcyclohexane, and 1,2-diethylbenzene, small quantities of *trans*-decalin and naphthalene, and n-decane. The formation of 1,2-diethylcyclohexane and 1,2-diethylbenzene can apparently be attributed to hydrogenolysis of the five-membered ring to decahydroazulene, with subsequent isomerisation of the seven-membered ring.

As expected from the conformational characteristics of cyclodecane, the chief direction of its transformations proved to be the transannular C_5-dehydrocyclisation into decahydroazulene. n-Decane—the product of the direct hydrogenolysis of the ten-membered ring—made up 13% of the weight of the catalysate[14]:

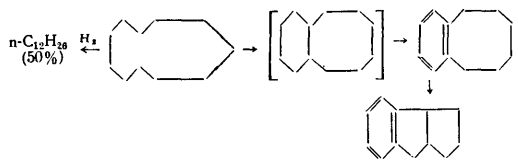


There are no published data on the conformational characteristics of an eleven-membered ring. Transannular reactions are characteristic of cycloundecane compounds, however, just as they are for 8–10-membered cyclic compounds[15]. Therefore cycloundecane apparently has transannular hydrogen atoms close to one another, so that for this compound, as for the cyclanes examined above, transannular dehydrocyclisation should take place readily. In contact with platinised carbon at 300°C, cycloundecane reacted to give 15% direct hydrogenolysis of the ring with the formation of n-undecane and dehydrocyclisation into *trans*-bicyclo[5,4,0]undecane, which under the conditions of the experiment was then converted into benzosuberane. The appearance of small quantities of α-methylnaphthalene and naphthalene in the catalysate can be attributed to isomerisation of the seven-membered ring into bicyclo[5,4,0]undecane with the formation of 1-methyldecalin and 9-methyldecalin, which then undergoes dehydrogenation under the conditions of the experiment:



Study of the structure of cyclododecane (Fig. 3) showed that there is no significant transannular interaction between opposite hydrogen atoms, and that the shortest distance between the hydrogen atoms is 2.1 Å. If it is assumed that transannular dehydrocyclisation takes place with the removal of the hydrogen atoms closest to one another, increase in the dimensions of the ring and increase in the distance between the transannular hydrogen atoms should decrease the ability of the cyclane to undergo transannular dehydrocyclisation.

In actual fact, it was found that the dehydrocyclisation of cyclododecane takes place to the extent of only 50%, with the formation of bicyclo[6,4,0]dodecane, which on dehydrogenation is converted into benzocyclo-octane; the latter, like cyclo-octane[5,6], is then converted into benzopentalane, the yield of n-dodecane amounting to 50%.[16]



Thus the catalytic transformations of hydrocarbons containing rings of medium dimensions in the present of platinised carbon at 300°C take place in two main directions:

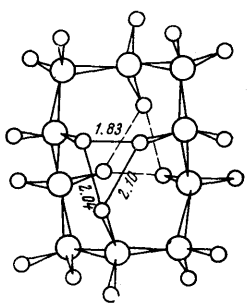


Fig. 2. Conformation of cyclodecane.

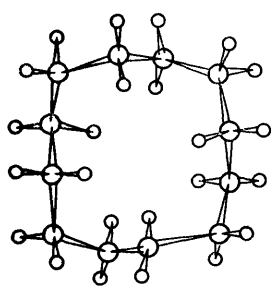


Fig. 3. Conformation of cyclododecane.

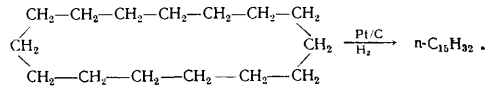
transannular dehydrocyclisation with the formation of condensed aromatic and non-aromatic hydrocarbons, and direct hydrogenolysis of the ring with the formation of normal paraffinic hydrocarbons. This last observation is of fundamental importance, since until recently hydrogenolysis in the presence of platinised carbon was known only for rings containing not more than five carbon atoms.

In 1962 it was shown that the products of the transformations of cycloheptane in the presence of platinised carbon at 300°C include n-heptane, from which it follows that the seven-membered ring also undergoes direct hydrogenolysis [17]. Liberman and coworkers [18] showed that cyclohexane does not undergo ring opening in the presence of a platinum catalyst, but hydrogenation of the six-membered ring is observed with ruthenium, iridium, and osmium, deposited on carbon.

The ability of the cyclane with a ring of medium dimensions to undergo hydrogenolysis in the presence of a platinum catalyst increases from cyclo-octane to cyclododecane; with the twelve-membered ring, the degree of hydrogenolysis increases sharply and the yield of normal alkane reaches 50%. The ability of the cyclane to undergo transannular dehydrocyclisation changes in the opposite sequence: the transannular dehydrocyclisation of cyclo-octane takes place to the extent of almost 100%, that of cycloundecane to the extent of 85%. and that of cyclododecane to the extent of only 50%. The structures of the resulting bicyclic hydrocarbons are determined by the conformational characteristics of the original cyclanes.

The hydrogenolysis and transannular dehydrocyclisation which take place in a number of medium-sized rings in the presence of a platinum catalyst are apparently competing reactions: for 8–10-membered cyclanes, because of their conformational characteristics, dehydrocyclisation takes place readily, and the rate of dehydrocyclisation is greater than the rate of hydrogenolysis, whereas with cyclododecane, which does not have such a favourable structure for dehydrocyclisation, the rates of the two reactions become commensurate. With large rings, the appreciable dimensions of the ring and the fact that there are no opposed hydrogen atoms at a short distance from one another should hinder intramolecular dehydrocyclisation, and hydrogenolysis may become the chief reaction.

As a representative of hydrocarbons containing rings with large dimensions, we took cyclopentadecane. It was found that cyclopentadecane in the presence of platinised carbon at 300°C in fact undergoes only hydrogenolysis of the ring with the formation of n-pentadecane as the only reaction product [19].



The dependence of the degree of hydrogenolysis on the number of units in the ring is shown in Fig. 4.

Usually, in the discussion of the reactivity of cyclic compounds containing rings with medium dimensions, allowance is made for the change in the strain, in addition to other factors characteristic of the given reaction. The problem of the strain in medium-sized rings is extremely complex. In its examination, allowance must be made for three factors: the distortion of the valency angles, producing Bayer strain, the energy of the torsion angles—Pitzer strain—and the transannular interaction of atoms which are not joined to one another.

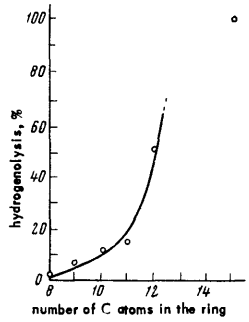


Fig.4. Dependence of the degree of hydrogenolysis on the number of C atoms in the ring.

X-Ray diffraction study of the structures of 8-, 9-, 10-, and 12-membered rings has provided a picture of the strain in these rings. The structure of the eight-membered ring has been described in less detail, but for the others, as already noted, the values of the C–C–C valency angles, the torsion angles, and the shortest distance between the transannular hydrogen atoms have been calculated.

From these data it may be concluded that among the medium-sized rings, the greatest strain should be shown by cyclononane and cyclo-octane, since they are characterised by considerable Bayer and Pitzer strain, and also by strain due to transannular interaction. Cyclodecane has almost no Pitzer strain, but its valency angles are much greater than tetrahedral, indicating appreciable Bayer strain. Cyclodecane is also characterised by strain due to transannular interaction. Unfortunately, the structure of cycloundecane has not been studied, but on the basis of the heat of combustion [20], which may give information on the strain in cyclic compounds, it may be concluded that cycloundecane is not free from strain, and that, like cyclodecane, it is apparently characterised by strain due to transannular interaction. X-Ray diffraction study shows that in cyclododecane there is no Pitzer or Bayer strain, nor significant transannular interaction. Cyclopentadecane is free from all forms of strain.

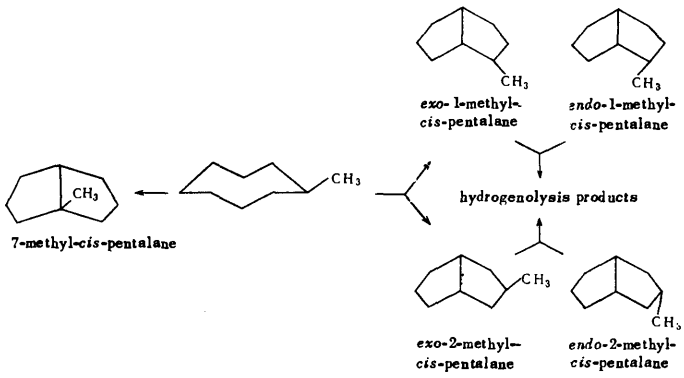
Examination of the above material in the light of modern views on ring strain indicates that the formation of a bicyclic hydrocarbon by intramolecular dehydrocyclisation removes the transannular strain produced as a result of the repulsion of opposite hydrogen atoms and hence is energetically favourable for 8–11-membered cyclanes. For cyclododecane, in which there is no significant transannular interaction, dehydrocyclisation will not be so energetically favourable as for the other cyclanes with medium-sized rings. In actual fact, cyclo-octane undergoes dehydrocyclisation to the extent of almost 100%, cyclononane to the extent of 93%, and cyclododecane to the extent of only 50%.

In hydrogenolysis, the chief role is apparently played not by the strain in the original molecule but by the strain produced in the transition complex when the cyclane molecule is adsorbed on the catalyst surface.

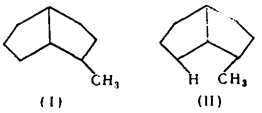
To investigate the influence of an alkyl substituent on the direction of the transformation of hydrocarbons with medium-sized rings, a study was made of the behaviour of methylcyclo-octane, methylcyclononane, and methylcyclodecane in the presence of platinum catalysts [21,22].

On platinised carbon at 300°C, methylcyclo-octane, like cyclo-octane itself, shows only slight (~ 1%) direct hydrogenolysis of the ring with the formation of isomeric methyloctanes. The chief reaction undergone by methylcyclo-octane under the above conditions is C_5-dehydrocyclisation, leading to the formation of all isomeric methyl-*cis*-pentalanes. Of these, 1-methyl-*cis*-pentalane is formed preferentially, and 2-methyl-*cis*-pentalane and 7-methyl-*cis*-pentalane are formed in smaller quantities. The catalysate also contains products of the hydrogenolysis of the methylpentalanes; to decrease the amount, the methylcyclo-octane was subjected to catalysis on a specially selected platinum catalyst containing 2% iron[23]. An interesting feature is that in this instance the formation of isomeric methylpentalanes in the same proportions as on platinised carbon is observed.

The ratio of methyl-*cis*-pentalanes formed by the transannular dehydrocyclisation of methylcyclo-octane does not depend on the nature of the platinum catalysts studied and is apparently determined by the conformational characteristics of the methylcyclo-octane molecule.

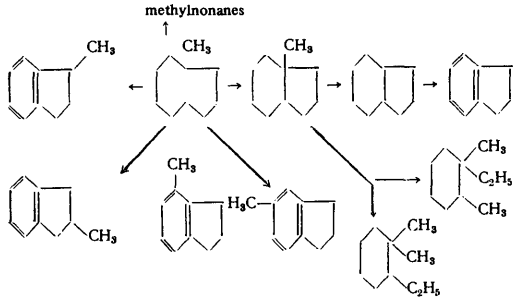


Another noteworthy feature is that, of the *exo*- and *endo*-1-methyl-*cis*-pentalanes formed, the *exo*-isomer predominates, whereas *exo*- and *endo*-2-methyl-*cis*-pentalanes are formed in comparable quantities. The preferential formation of the *exo*-form of 1-methyl-*cis*-pentalanes (I) relative to the *endo*-form (II) is apparently due to the characteristic features of the three-dimensional structure of this hydrocarbon. In the *endo*-form the methyl group and the hydrogen attached to the sixth carbon atom come so close together that the forces of repulsion between them make this form of the molecule more strained than the *exo*-form. In 2-methyl-*cis*-pentalane the *endo*- and *exo*-forms of the molecule have equally favourable arrangements of the methyl group, so that these isomers are apparently equally stable, and the *exo*- and *endo*-forms of 2-methyl-*cis*-pentalane are formed in almost equal quantities.



The chief primary product of the transformations of methylcyclononane in the presence of a platinum catalyst was *cis*-8-methylhydrindane; this hydrocarbon and the products of its secondary transformations made up ~ 50% of the weight of catalysate. 8-Methylhydrindane could be formed by the transannular dehydrocyclisation of methylcyclononane only if the methyl group is attached to a carbon atom with an intra-annular hydrogen atom which is moved closer, in the 1,5 position, to an intra-annular hydrogen atom of the opposite carbon atom. The removal of a methyl group in 8-methylhydrindane leads to the formation of hydrindane, and the dehydrogenation of the six-membered ring in hydrindane produces indane. Ethyldimethylcyclohexanes are formed as a result of the hydrogenolysis of the five-membered ring in 8-methylhydrindane.

Thus methylcyclononane is characterised by a type of transannular dehydrocyclisation which takes place preferentially with the participation of the hydrogen attached to the carbon atom of the ring carrying the substituent. The presence of 1-, 2-, 4-, and 5-methylindanes in the catalysate, however, indicates that other intra-annular hydrogen atoms, brought closer together in the 1,5 position, may also take part in this reaction. The catalysate contained isomeric methylnonanes, formed by the direct hydrogenolysis of the nine-membered ring in the same amounts as the n-nonane in the catalytic transformations of cyclononane.



The chief primary reaction of methylcyclodecane in the presence of platinised carbon is transannular dehydrocyclisation, which takes place in two directions: firstly, C_5-dehydrocyclisation takes place with the formation of methyldecahydroazulenes, and secondly, C_6-dehydrocyclisation takes place, producing methyldecalins and methylnaphthalenes. Like cyclodecane, methylcyclodecane is characterised to a greater extent by C_5-dehydrocyclisation than by C_6-dehydrocyclisation, since the products formed by the first reaction make up more than 70% of the total weight of transformation products.

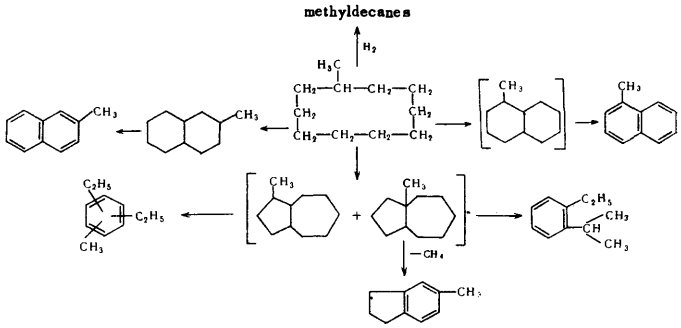
Methyldecahydroazulenes are unstable under the conditions of the experiment and undergo further transformation. Secondary transformations of the methyldecahydroazulenes

TABLE. Composition of the products of the transformation of methylcyclo-octane at 800°C.

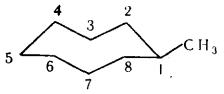
Hydrocarbons	Percentage concentration	
	Pt/C	Pt/Fe/C
Methyloctanes	1	>1
7-Methyl-*cis*-pentalane	8	13
endo-1-Methyl-*cis*-pentalane	6	8
exo-1-Methyl-*cis*-pentalane	34	35
endo-2-Methyl-*cis*-pentalane	11	15
exo-2-Methyl-*cis*-pentalane	17	18
Products of the hydrogenation of methyl-*cis*-pentalanes		
I- and 2-Methylpentalanes	12	11
7-Methylpentalane	11	

apparently lead to the formation of 1-ethyl-2-isopropylbenzene, which makes up almost half of the weight of the methylcyclodecane transformation products. Of all the possible isomers of methyldecahydroazulene, only 9-methyldecahydroazulene and 1-methyldecahydroazulene can lead to the formation of 1-ethyl-2-isopropylbenzene as a result of hydrogenolysis of the five-membered ring and isomerisation of the seven-membered ring. Secondary transformations of these hydrocarbons may also explain the presence of diethylmethylbenzene and 5-methylindane in the catalysate.

Thus the final products of the transformations of methylcyclodecane indicate that on transannular C_5-dehydrocyclisation of this hydrocarbon not all the isomeric methyldecahydroazulenes are formed to equal extents, and that 9-methyldecahydroazulene and 1-methyldecahydroazulene apparently predominate. The presence of isomeric methyldecanes in the catalysate indicates direct hydrogenolysis of the ten-membered ring. Comparison of the degrees of hydrogenolysis of cyclodecane and methylcyclodecane indicates that cyclodecane itself undergoes hydrogenolysis more readily than its homologue: the yield of paraffinic hydrocarbons for methylcyclodecane amounts to only 2% of the weight of transformation products, whereas for cyclodecane under the same conditions, 13% n-decane is formed:



Transannular dehydrocyclisation in the series of alkylcyclanes with medium-sized rings is directed in character: the preferential direction of this process is not determined by the hydrogen atom attached to the tertiary carbon atom of the ring but is apparently related to the conformational characteristics of the cyclanes. In fact, in the dehydrocyclisation of methylcyclo-octane, the formation of 1-methylpentalane predominates, whereas from methylcyclononane under the same conditions, the bicyclic hydrocarbon with angular arrangement of the methyl group is formed preferentially, and the dehydrocyclisation of methylcyclodecane apparently produces chiefly 9- and 1-methyldecahydroazulenes. In the transannular dehydrocyclisation of methylcyclo-octane



there are two possibilities for the formation of 1-methylpentalane: by the removal of two quasi-axial hydrogen atoms attached to $C_{(2)}$ and $C_{(6)}$ or $C_{(4)}$ and $C_{(8)}$, and one possibility each for the formation of 2- and 7-methylpentalane (removal of the hydrogen on $C_{(3)}$ and $C_{(7)}$ for 2-methylpentalane and on $C_{(1)}$ and $C_{(5)}$ for 7-methylpentalane). If it is assumed that these possibilities for the formation of methylpentalanes are equally probable, the quantity of 1-methylpentalane in the methylcyclo-octane catalysate should have been double the quantities of 2- or 7-methylpentalane. In fact, 1-methylpentalane predominates in the catalysate for this reaction.

In cyclononane (see Fig. 1) the substituents probably can occupy only the extra-annular positions. Data obtained by X-ray diffraction studies show that substituents are preferred among the extra-annular positions. An example is the position of the substituent on $C_{(1)}$. The preferential positioning of the methyl group in the nine-membered ring also apparently explains the preferential formation of 8-methylhydrindane in the transannular dehydrocyclisation of methylcyclononane. The methyl group is attached to the carbon atom carrying an intra-annular hydrogen atom which has been brought closer to the intra-annular hydrogen atom of the opposite carbon atom of the ring. The transannular dehydrocyclisation apparently takes place with the removal of the intra-annular hydrogen atoms which have been brought together with the production of a new C–C bond.

Analogous reasoning can be applied to methylcyclodecane, in which directed transannular dehydrocyclisation is also observed, with the preferential formation of 9- and 1-methyldecahydroazulenes as primary reaction products.

The transformations of hydrocarbons with medium-sized rings in the presence of a platinum catalyst take place in two independent directions: transannular dehydrocyclisation and direct hydrogenolysis of the ring. The first stage of the transannular dehydrocyclisation leads to the formation of a bicyclic hydrocarbon, whose nature is determined chiefly by the conformational characteristics of the original cyclane. Under the conditions of the experiment, bicyclic hydrocarbons undergo further transformations: aromatisation, hydrogenolysis of five-membered rings, and isomerisation of seven-membered rings, to give reaction mixtures with extremely complex compositions. For methylcyclanes with 8–10-membered rings, transannular dehydrocyclisation is directed in character; the preferential direction of the catalytic process is determined by the conformation of the original hydrocarbon.

With increase in the dimensions of the ring there is a decrease in the extent to which transannular dehydrocyclisation takes place and an increase in the extent to which hydrogenolysis takes place; for large rings, hydrogenolysis becomes the main direction of the transformations. These data show that hydrogenolysis is general in the chemistry of cyclic hydrocarbons: hydrogenolysis is the only direction of the transformations for rings containing not more than five carbon atoms, and takes place in addition to dehydrocyclisation in medium-sized rings.

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TEMPERATURE DEPENDENCE OF THE RATE OF GAS-PHASE REACTIONS

V.N.Kondrat'ev and E.E.Nikitin

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1. INTRODUCTION

The rate constant of an elementary chemical reaction is usually expressed in the form of the Arrhenius equation:

$$k = A\exp(-E_0/kT) \qquad (1.1)$$

(where A and E_0 are constants) or of the formula

$$k = A_0T^{1/2}\exp(-E_0/kT), \qquad (1.2)$$

which follows from kinetic theory for when the activation energy is provided by the component of the kinetic energy of the relative motion of the interacting particles lying along the line of their centres[1]. Formula (1.2) can be obtained also in the more general example by assuming a particular dependence of the reaction cross-section upon the energy of relative motion[2]. Kassel[3] proposed also an empirical formula of the type:

$$k = CT^m\exp(-E_0/kT) \qquad (1.3)$$

($m > 0$), and gave some theoretical justification for it.

The dissociation rate constant is also frequently expressed in the form

$$k_d = A_0T^{-n}\exp(-D/kT), \qquad (1.4)$$

which takes account of the contribution of internal degrees of freedom to the activation of the molecule undergoing dissociation[1].

The rate constant of the recombination process, which is the reverse of the dissociation process, is most often described by the formula:

$$k_r = A_0T^{-m}. \qquad (1.5)$$

Whereas the formulae describing the rate constants of the dissociation and recombination processes have recently achieved some—but far from complete—theoretical justification, as discussed below, exchange processes on the other hand have hardly been investigated at all in spite of the fact that they are the commonest type of elementary reaction. Yet, it is possible to introduce some significant advances into the quantitative kinetics of exchange processes on the basis of the (still imperfect) theory of the transition state alone, and also on the basis of quantum statistics.

The main problem in the theoretical calculation of the rate constant is to evaluate the contribution of the various degrees of freedom and to make allowance for the perturbation of the equilibrium distribution brought about by the reaction itself. The transition state method avoids both these difficulties by assuming that the complicated energy exchange process can be described by the motion of the representative point along some reaction coordinate q_γ whose choice is not strictly unique, whilst completely ignoring the perturbation of the equilibrium distribution of the reactants over the states. To some extent, correct allowance for these two factors can be made independently. First, we calculate the reaction cross-section σ_γ as a function of the dynamic parameters of the partners during a collision—the initial vibrational states n_i and rotational states j, and also the relative velocity v of the colliding molecules. As a second step, the reaction rate R is calculated by averaging σ_γ over all the n, j, v initial states by means of the expression

$$R = \int \sigma_r(n, j, v)\, v f(n, j, v)\, d\Gamma. \qquad (1.6)$$

Here $f(n, j, v)$ is the distribution function (in general, non-equilibrium) of the colliding molecules, normalised for the total number of reacting molecules. If the concentrations of the initial molecules are taken out of f as common factors, the reaction rate R can be expressed in the form

$$R = k(C_A)^\alpha(C_B)^\beta \qquad (1.7)$$

where k now has the significance of the rate constant of a reaction of order α with respect to reactant A, of order β with respect to reactant B, etc. The calculation of the

function f in expression (1.6) becomes a statistical problem which can be solved by examining the system of equations describing at the same time the relaxation (that is, the transitions between the various energy states of the reacting molecules) and the true chemical reaction (that is, the regrouping of atoms upon collision of the molecules).

Both these factors (the contribution of different degrees of freedom and the perturbation of the equilibrium distribution) influence the temperature dependence of the rate constant, and hence it is important to resolve explicitly the dynamic and the static parts of the pre-exponential factor of dissociation rate constants in order to understand the mechanism of the elementary act. In what follows, we shall briefly discuss the temperature dependence of dissociation, recombination, and exchange reactions in the gas phase.

2. DISSOCIATION

It is well established that the thermal dissociation of molecules is kinetically characterised by a first-order law at high pressures and by a second-order law at low pressures[4]. Between these two extremes is found a transition region of pressures where the reaction order varies from first to second. The pressure dependence of the dissociation rate constant arises, essentially, from the disturbance of the equilibrium distribution over the internal degrees of the reacting molecules. Since the extent of this disturbance varies with pressure, it is desirable to consider separately the possible limiting cases of the reaction

$$AB+M\rightarrow A+B+M \qquad (2.1)$$

First-Order Reactions

It is evident from physical considerations that at high pressures, when the rate of intermolecular energy transfer is greater than the rate of intramolecular energy transfer, the disturbance of the equilibrium distribution is a minimum†. Therefore we must assume that here the transition state method should lead to a satisfactory approximation for the rate constant k of the reaction. The general expression for k within the limits of this approximation is[6]

$$(k_d)_\infty = g^+\chi\frac{kT}{2\pi\hbar}\frac{F^+_{AB}}{F_{AB}}\exp(-E_0/kT), \qquad (2.2)$$

where F_{AB} and F^+_{AB} are the partition functions of the stable and the activated molecule, g^+ is the number of independent decomposition paths, and χ is the transmission coefficient.

† Throughout this paper we shall assume, when dealing with the mechanism of intramolecular energy transfer in an active molecule, that the statistical approximation is applicable. According to the modern concepts of the statistical theory[4,5] of unimolecular reactions, all the degrees of freedom of active and of activated molecules can be classified into inactive, adiabatic, and active. The first do not generally take part in energy redistribution and they do not appear explicitly in the expression for the rate constant. As regards the second, it is assumed that during the intervals between collisions the quantum numbers which characterise these degrees of freedom do not alter, but on going from an active to an activated molecule a change in these degrees of freedom is assumed—in particular, a change from vibrations to rotations[5].

The factor F^+_{AB} can be said to be known if the configuration of the activated molecule is known, or alternatively if the critical surface S^+ in (A + B) phase space is known, since its intersection with the representative point can be identified with the completion of the elementary chemical act. If we adopt a system of harmonic oscillators as a model of the molecule, and the transmission coefficient is close to unity, it follows from Eqn. (2.2) that at high temperatures ($kT \gg \hbar\omega_i$) the pre-exponential factor is of the same order as the molecular vibration frequency. Furthermore, using the theory of small vibrations it can be shown that the term $\frac{kT}{2\pi\hbar}\frac{F^+_{AB}}{F_{AB}}$ in Eqn. (2.2) always falls between the lowest and the highest frequency of the active molecule. Nevertheless, the general treatment in principle does not set an upper limit to the pre-exponential factor. However, since the frequency factor of the majority of experimentally investigated uni molecular reactions is found to be of the same order as the vibration frequency, reactions whose pre-exponential factor is greater than 10^{14} s^{-1} are often treated in the literature as having an anomalously high pre-exponential factor. High pre-exponential factors are associated with the appearance of a high degree of anharmonicity in the internal vibrations of the molecule. Anharmonicity loosens the intramolecular bonds and leads to the formation of a weakly bound activated molecule. This effect is often referred to as a large entropic contribution by the activated molecule to the partition function F^+.

The simplest (and from the quantitative aspect the most important) manifestation of anharmonicity during dissociation is the conversion of various types of vibration of the active molecule into free rotation of the activated molecule.

We can make an order-of-magnitude estimate of the contribution made by the conversion of one vibrational degree of freedom of the AB molecule into a rotational degree of freedom of the activated molecule. Under classical conditions ($kT \ll \hbar\omega_i$) we have

$$F_{vibr} = kT/\hbar\omega,\ F_{rot} = (2IkT)^{1/2}/2\pi\hbar\,. \qquad (2.3)$$

Calculation of the frequency on the basis of the Morse potential leads to $\frac{F_{rot}}{F_{vibr}} \simeq (D/kT)^{1/2}$, where D is the energy of the chemical bond.

As an example of a reaction with an anomalously large frequency factor we may consider the thermal dissociation of ethane into two CH_3 radicals. The calculation by Setser and Rabinovitch[7] uses a model of the C_2H_6 molecule in the activated state involving 12 oscillators (2 non-interacting CH_3 radicals) and 5 active rotators (free internal rotation of the CH_3 groups about the C–C axis and 4 degrees of freedom corresponding to the swing of the planes of the H_3 atoms of each CH_3 group). The C–C bond is chosen as the reaction coordinate. The calculation leads to a pre-exponential factor for the reaction of 10^{17} s^{-1} at 600°C. This figure agrees with the value derived from the experimental bimolecular recombination constant by using the relationship between the dissociation and recombination constants given by the equilibrium constant.

Formula (2.2) for the rate constant k_∞ is strictly accurate if the quantity F_{AB} is taken to be the total partition function of the activated molecule. When the problem is formulated in this way the whole of the difficulty attending the calculation of the constant is transferred to a correct definition of the critical surface. This task is generally extremely complex. Therefore in every instance when the critical surface is determined from simple qualitative

considerations a factor χ, which makes allowance for the repeated passage of a representative point through the critical surface, is introduced. Exact calculation of χ is equivalent to solving the many-body problem. An attempt to solve this problem is equivalent to denying the simplifying assumptions associated with the introduction of a reaction coordinate. However, since the latter approach is thought to be justified, we shall use the expression for χ (and discuss the temperature dependence of the transmission coefficient) which applies to the one-dimensional model.

For adiabatic reactions, assuming negligible contribution of the tunnel effect, we can put $\chi = 1$. For non-adiabatic reactions involving a change in electronic state the situation $\chi \ll 1$ is entirely possible. In this case we obtain the following expression for χ on the basis of the Landau–Zener formula[8]:

$$\chi = 2\pi W^2/\Delta F\hbar\,(kT/2\pi\mu)^{1/2}\,, \qquad (2.3a)$$

where μ is the effective mass corresponding to the motion along the reaction coordinate, ΔF is defined by the difference between the slopes of the intersecting terms U_1 and U_2 ($\Delta F = |dU_1/dq_1 - dU_2/dq_2|$); W is the matrix element which connects the relevant electronic energy levels. If the connection is through spin–orbital interaction, W is independent of T, and Eqn. (2.3a) leads to the expression

$$\chi(T) \simeq T^{-1/2}\,. \qquad (2.4)$$

If the non-adiabatic connection is due to Coriolis forces acting on the electrons, W is proportional to the speed of rotation of the molecule, so that $W^2 \simeq T$. Hence, from (2.3), we have

$$\chi(T) \simeq T^{1/2}\,. \qquad (2.5)$$

The tunnel corrections, which alter the value of χ when quasi-classical conditions cease to apply to the motion of the representative point near the critical surface, have different forms for adiabatic and non-adiabatic reactions. For the former, the tunnel correction arises from the penetration of the particle under a potential barrier which is approximately parabolic (at least, near the top of the barrier), and the approximate expression for χ is of the form[9]

$$\chi(T) \simeq (\hbar\omega^*/2kT)\sin(\hbar\omega^*/2kT)\,, \qquad (2.6)$$

where ω^* denotes the vibration frequency close to the minimum of the "inverted" potential hump.

In the second instance, penetration by the tunnel effect takes place below the point of quasi-intersection of the terms, and the shape of the barrier is nearer to triangular than to parabolic. Under these conditions χ is described[10] as the product of the over-the-barrier transmission coefficient (2.3a) and an exponential tunnel correction:

$$\chi(T) = \frac{2\pi W^2}{\Delta F\hbar\,(kT/2\pi\mu)^{1/2}}\exp\left[\frac{1}{12}(\varepsilon/kT)^3\right],\quad \varepsilon = \left[\hbar\,\frac{\partial U_1}{\partial q_1}\frac{\partial U_2}{\partial q_2}\Big/\sqrt{2\mu\Delta F}\right]^{2/3}. \qquad (2.7)$$

Evidently, a situation in which $\chi > 1$ becomes possible if tunnel transmission is taken into account. In other words, the effective activation energy becomes lower than the energy E_0 of the potential barrier. The correction for barrier lowering has a complicated temperature dependence, and it is therefore assigned to the pre-exponential factor.

Calculation of the statistical summations in (2.2) leads to the following formulae for the temperature dependence of the pre-exponential term if the model of the dissociating molecule is set up in terms of a system of s oscillators and r rotators and that of the activated molecules in terms of s^+ oscillators and r^+ rotators:

$$A(T) \simeq \chi(T)\,T^{(r^+-r/2)+1},\ \hbar\omega_i,\ \hbar\omega_i^+ \gg kT \qquad (2.8)$$

$$A(T) \simeq \chi(T)\,T^{(r-r^+)/2},\ \hbar\omega_i,\ \hbar\omega_i^+ \ll kT \qquad (2.9)$$

with $r^+ > r$ in most cases. Thus, leaving aside the transmission coefficient χ, the quantity A is characterised by a positive temperature dependence at low temperatures and a negative (or zero for $r^+ = r$) temperature dependence at high temperatures.

Second-Order Reactions

At low pressures the rate of decomposition is substantially influenced by the disturbance of the Boltzmann distribution over the internal degrees of freedom of the decomposing molecule. Hence the transition state method cannot be used to calculate the rate constant k of the reaction. For the same reason, the temperature dependence of $A(T)$ can be calculated only if the detailed excitation mechanism of the molecule AB to the dissociation threshold is known, since in the low-pressure region the rate of decomposition is limited by the rate of vibrational relaxation of excited vibrational states. Since we still lack adequate information on the probability of energy exchange during the collision of vibrationally excited molecules, we may conveniently consider the two limiting cases of activation which allow k_d to be calculated in a closed form and lead to a number of conclusions on the temperature dependence of A.

These limiting cases are known in the literature as the strong collision mechanism and the stepwise excitation mechanism[5]. The former mechanism assumes that the AB molecules which decompose at low pressures are those with energy $E_{vibr} > D$ (the active AB* molecules), and that the rate of deactivation of the active molecules does not depend on their state and is determined by the effective number of collisions between AB* and M per unit time. In this instance the principle of detailed balance requires a rate of decomposition, identical to the rate of excitation to energy states $E_{vibr} > D$, given by

$$k_d = Z\int_D^\infty \rho(E)\exp(-E/kT)\,dE/F_{AB}\,. \qquad (2.10)$$

In this excitation mechanism the dissociation produces a disturbance of the equilibrium distribution only above the threshold level. For $E_{vibr} < D$ the vibrational distribution function retains its equilibrium value.

In the stepwise excitation mechanism it is assumed that each collision between AB and M transfers an amount of energy small compared to the dissociation energy D. Thus, the molecules which react at low pressures have approached the energy threshold from below, and the concentration of active molecules is negligibly small.

If excitation of the AB molecules occurs as a result of single-step vibrational transitions ($n \to n+1$) the expression for k_d has the form

$$k_d = Z_0\left[\sum_{n=0}^{N}\exp[E_n/kT]/P_{n,n-1}\right]^{-1}\Big/F_{AB}\,; \qquad (2.11)$$

N is the number of the level corresponding to the dissociation threshold, and $P_{n,n-1}$ is the transition probability referred to a single gas-kinetic collision. For ease of comparison with (2.10), this expression can be transformed

in a way which allows generalisation to many-quantum transitions and contains as a parameter the mean square of the energy transferred at each collision $\langle\Delta E^2\rangle$. By definition we have

$$\langle\Delta E^2\rangle = (\Delta E_{n-1,n})^2 P_{n-1,n} + (\Delta E_{n,n+1})^2 P_{n,n+1} . \quad (2.12)$$

Assuming that the transition energy $\Delta E_{n,n-1}$ is an insensitive function of n, Eqn. (2.12) can be rewritten in the form

$$\langle\Delta E^2\rangle = 2\,(\Delta E_{n,n-1}^2)^2\, P_n , \quad (2.13)$$

where we have used the terminology $P_n \simeq P_{n,n-1} \simeq P_{n,n+1}$. Substituting P_n from (2.12) into (2.11) and replacing the summation by an integral (which is permissible for $\langle\Delta E^2\rangle^{1/2} \ll kT$) we find

$$k_d = Z_0\left[\int_0^D \exp(E/kT)\frac{2dE}{\rho(E)\,\langle\Delta E^2(E)\rangle}\right]^{-1}\Big/F_{AB} . \quad (2.14)$$

It is assumed that the density of levels $\rho(E)$ is related to ΔE by $\rho(E) \simeq (\Delta E)^{-1}$. The quantity $\langle\Delta E^2\rangle$ in (2.14) is equivalent to a diffusion coefficient of the representative point over the energy levels. Hence we may suggest that Eqn. (2.14) will be correct also for many-quantum transitions provided that the excitation process can be described by the Fokker–Planck equation in energy space. Following Pitaevskii[11], we may test this assumption by direct integration of the equation as given, for example, by Nikitin[5].

The conditions under which the diffusion equation is applicable, already used above, are defined by the inequality $\langle\Delta E^2\rangle \ll (kT)^2$.

Comparing (2.14) with (2.10) we see that in the stepwise dissociation mechanism it is only molecules below the dissociation threshold ($E_{vibr} < D$) which contribute to the rate of decomposition. Thus, decomposition leads to zero population of the active molecule states and to breakdown of the equilibrium distribution below the F threshold[5]. The actual mechanism of the activation is intermediate between the two discussed above, and in general the rate of decomposition will be affected by the distribution of molecules both above and below the threshold.

By separating the exponential term from (2.10) and (2.14) we arrive at the following expressions for the pre-exponential term

$$A_1 = Z_0\int_0^\infty \rho(D+\varepsilon)\exp(-\varepsilon/kT)\,d\varepsilon/F_{AB} \quad (2.15)$$

$$A_2 = Z_0\left[\int_{-\infty}^0 \exp(\varepsilon/kT)\frac{2d\varepsilon}{\rho(D+\varepsilon)\,\langle\Delta E^2(D+\varepsilon)\rangle}\right]^{-1}\Big/F_{AB} . \quad (2.16)$$

Eqn. (2.15) applies to the strong collision mechanism, whereas Eqn. (2.16) applies to the stepwise excitation mechanism. In these expressions the quantity ϵ is measured from the dissociation limit; Eqn. (2.16) also assumes that the lower integration limit in (2.14) is insignificant.

We shall now turn to the temperature dependence of the pre-exponential A in the decomposition of polyatomic molecules. The calculation becomes particularly simple when the molecule can be described with acceptable precision by a model consisting of a system of s harmonic oscillators and r rotators. In the semi-classical approximation we have

$$\rho(E) = \frac{F_{rot}}{(kT)^{s/2}}\,\frac{(E+E_z)^{s+r/2-1}}{\Gamma(s+r/2)\,\Pi\hbar\omega_i} \quad (2.17)$$

where the zero-point vibration energy E_z is expressed in terms of the vibration frequency ω_i of the molecule AB by the relation

$$E_z = \frac{1}{2}\sum_i \hbar\omega_i \quad (2.18)$$

and F_{rot} denotes the rotational partition functions. Inserting (2.17) into (2.15) and taking $\rho(D+\epsilon)$ out of the integral at the point $\epsilon = 0$, we obtain

$$A_1 = \frac{Zg_{el}}{(s+r/2-1)!}\,\frac{(D+E_z)^{s+r/2-1}kT^{1-r/2}}{\prod_{i=1}^{s}\hbar\omega_i}\prod_i[1-\exp(-\hbar\omega_i/kT)]. \quad (2.19)$$

In this expression we have placed in evidence the term g_{el}, which allows for the contribution of electronically excited states lying below the dissociation threshold to the rate of decomposition. Formula (2.19) is correct within the following limitations, which are necessary to justify the use of Eqn. (2.17) and the approximation made in the integration of Eqn. (2.14):

$$D \gg skT, \quad (2.20a)$$

$$D > \sqrt{s}E_z . \quad (2.20b)$$

Formal insertion of the limit $s \to 1$ in Eqn. (2.19) leads (for $\hbar\omega/kT \ll 1$) to the well-known formula of the simplest collision theory if we put $g_{el} = 1$. This formula does not take account of the perturbation of the equilibrium distribution brought about by the decomposition.

In the classical limit Eqn. (2.19) leads to

$$A_1 \to Z_0 g_{el}\left(\frac{D+E_z}{kT}\right)^{s+r/2-1}\Big/\left(s-1+\frac{r}{2}\right)! \quad (2.21)$$

We now turn to a discussion of formula (2.16). In all real systems the functions $\langle\Delta E^2\rangle$ and $\rho(E)$ vary more slowly than exponentially for $E/kT \gg 1$. Hence, to evaluate the temperature dependence of A these functions can be taken out of the integral at the point $E = E_0$, that is, we can assign the energy transferred and the density of levels to states lying below the dissociation boundary by an amount kT. This leads to the expression

$$A_2 = Z_0 g_{el}\,\frac{\langle\Delta E^2\rangle}{(kT)^2}\,\rho(E_0-kT)\,\delta E\prod_{i=1}^{s}[1-\exp(-\hbar\omega_i/kT)]. \quad (2.23)\ddagger$$

In this expression the energy interval δE, which characterises the width of the region in which the equilibrium distribution is substantially disturbed, can be determined only by evaluating the integral in (2.16). As applied to the oscillator model of a polyatomic molecule, Eqn. (2.23) can be re written

$$A_2 = Z_0 g_{el}\,\frac{1}{2}\,\frac{\langle\Delta E^2\rangle}{kT}\,\frac{(E_0+E_r)^{s-1}}{\prod_{i=1}^{s}(\hbar\omega_i)}\prod_{i=1}^{s}[1-\exp(-\hbar\omega_i/kT)]. \quad (2.24)$$

In the classical limit ($\hbar\omega_i \ll kT$), expression (2.23) takes the form

$$A_2 = Z_0 g_{el}\,\frac{1}{2}\,\frac{\langle\Delta E^2\rangle}{(kT)^2}\left(\frac{E_0+E_n}{kT}\right)^{s-1}\Big/(s-1)! \quad (2.25)$$

Unlike formula (2.21), this expression contains the factor $\frac{1}{2}\langle\Delta E^2\rangle/(kT)^2$, which should be much smaller than unity as long as diffusion theory applies. However, if we put $\langle\Delta E^2\rangle \simeq (kT)^2$, Eqn. (2.25) is formally converted into (2.21). The temperature dependence introduced by this term cannot be established in general. A few conclusions

‡ No Eqn. (2.22) in Russian (Ed. of Translation).

are possible only if the anharmonicity of the vibrations is large, so that collisions have a high probability of leading to combination transitions in which various normal vibrations are excited and deactivated at the same time. No limits are imposed on the magnitude of the energy transferred. The only criterion which can probably be applied to evaluate $\langle\Delta E^2\rangle$ is the criterion put forward by Massey: the energy transferred with the highest probability is ΔE^*, defined by the condition

$$\Delta E^*/\hbar\alpha\bar{v} \sim 1 \qquad (2.26)$$

where $\bar{v}$ is the mean velocity of the colliding molecules and α^{-1} is the radius of action of the intermolecular potential. From (2.26) we arrive at

$$\langle\Delta E^2\rangle/(kT)^2 \sim \frac{1}{T} \qquad (2.27)$$

by putting $(\Delta E^*)^2 \simeq \langle\Delta E^2\rangle$ which is consistent with the condition (2.27). The stepwise excitation mechanism introduces an additional factor (T^{-1}) as compared with the strong collision mechanism.

These general ideas need to be made more precise before they can be applied to diatomic molecules. In general, there is no way of predicting which of the activation mechanisms will apply to the dissociation of diatomic molecules. Only in the simplest example—dissociation in an inert gas atmosphere—can we assert that excitation will be by the stepwise mechanism (see below). The non-equilibrium distribution function for vibrational states is zero at $E_{vibr} > D$ in the decomposition of diatomic molecules whatever the activation mechanism. Below the dissociation threshold the distribution function is close to its equilibrium value for strong collisions, and is very different from its equilibrium value (although it approaches it on moving away from the threshold) for stepwise excitation.

Expression (2.23) must be slightly modified for diatomic molecules. This is because rotation of the molecule causes significant distortion of the potential curve, thus altering the effective dissociation energy. Therefore, strictly speaking, the dissociation of a diatomic molecule cannot be described only in terms of diffusion in total energy space: we must also take into consideration diffusion in angular momentum space. In this instance, allowance for the rotational partition function F_{AB}^{rot} introduces into Eqn. (2.23) the factor g_{rot}, which has a weak temperature dependence ($g_{rot} \simeq T^{-1/2}$–$T^{-1/3}$). If the reduced mass of A and B is less than (or of the same order as) the reduced mass of AB and M, one-quantum transitions will take place up to the dissociation limit. Here we put $\langle\Delta E^2\rangle \simeq (\Delta E^*)^2$, $\rho(E_0 - kT) \simeq 1/\Delta E^*$. These lead to the expression

$$A_2 \simeq Z g_{el} g_{rot} \frac{\Delta E^*}{kT}[1 - \exp(-\hbar\omega/kT)]. \qquad (2.28)$$

In the opposite case, when dissociation of a heavy diatomic gas is proceeding in an atmosphere of a lighter gas, the average energy transferred $\langle\Delta E^2\rangle$ can be obtained (impulsive approximation) by considering the two-body collisions A–M and B–M. In this approximation we can write

$$\langle\Delta E^2\rangle \sim \frac{\mu_{AB-M}}{\mu_{AB}} E_{kin}^{AB}\, kT\,, \qquad (2.29)$$

where E_{kin}^{AB} is the mean kinetic energy of the nuclei of the AB molecules. A detailed investigation[12,13] has shown that the product $\rho(E)E_{kin}^{AB}$ close to the dissociation boundary, which appears in the general expression (2.23) for the rate constant, is relatively insensitive to the model chosen for the decomposing molecule. In particular, identical temperature dependences of A_2 are obtained for a chopped harmonic oscillator and for a Morse oscillator:

$$A_2^{harm} \sim A_2^{Morse} \sim Z g_{el} g_{rot}\,[1 - \exp(-\hbar\omega/kT)]\,. \qquad (2.30)$$

Formulae (2.18) and (2.30) have been obtained for different limiting assumptions regarding the parameter which determines the effectiveness of energy transfer—the ratio of the collision time $\tau \simeq 1/\alpha\bar{v}$ to the vibration period of the nuclei $1/\omega$. Hence we may assume that in all intermediate cases the temperature dependence of the pre-exponential term A describing the dissociation of diatomic molecules will be of the form

$$A \sim T^{1/2}[1 - \exp(-\hbar\omega/kT)]g_{rot}(T)\,. \qquad (2.31)$$

Experiments in shock tubes at high temperatures ($\hbar\omega/kT \ll 1$) lead to an expression of the type of (2.31) for the dissociation of diatomic molecules in an inert gas atmosphere. If, on the other hand, the dissociation takes place in an atmosphere of the diatomic gas or in an atmosphere of a monatomic gas of the same element (for example, dissociation of O_2 by O_2–O_2 and O_2–O collisions), the experimentally observed value of the factor A shows a stronger, negative temperature dependence than predicted by the above theory. A theoretical explanation of this discrepancy involves making allowance for energy transfer between the vibrational, rotational, and translational degrees of freedom of the reactants, and also evaluating possible non-adiabatic effects. Unfortunately, reliable calculations of these processes are still lacking.

Intermediate Pressure Region

In the transition region between first-order and second-order reactions the observed rate of decomposition is determined by competition between intermolecular and intramolecular energy exchange processes. Therefore, in addition to the considerations of activation and deactivation mechanisms discussed above, the theory must include assumptions on the kinetics of energy redistribution within the molecule. These kinetics are characterised by the distribution function $h(\tau)$ of active molecules over the relaxation times τ. The available information on the function $h(\tau)$ is mainly based on a theoretical study of model systems and does not allow us to relate the distribution function uniquely to the dynamic characteristics of real molecules[14]. Therefore, calculations of the constant k in the intermediate pressure region usually involve the assumption of instantaneous statistical redistribution of the energy within the molecules§. This is equivalent to assuming an exponential form of the function $h(\tau)$:

$$h(\tau) = k(E)\exp[-k(E)\tau]\,, \qquad (2.32)$$

where $k(E)$ is the rate constant of the spontaneous decomposition of the active molecule. If we adopt the hypothesis (2.32), we can find the rate constant $k(E)$ by solving the kinetic equations describing the spontaneous decomposition and relaxation in terms of the two alternative activation mechanisms. Of course, the strong collision mechanism and the stepwise activation mechanism lead to different general expressions for $k(T)$. We note only that a relatively simple formula, often used to interpret experimental

§ The term instantaneous in this context means that the characteristic time for the statistical redistribution is much smaller than the time between successive collisions.

results, can be obtained solely from the strong collision mechanism. It is of the form

$$k = \frac{kT}{2\pi\hbar}\frac{F_1^+}{F_1F_2}\exp(-E_0/kT)\int_{E^+=0}^{\infty}\frac{g^+W_2^+(E^+)\exp(-E^+/kT)\,dE^+/kT}{1+g^+W_2^+(E^+)/2\pi\hbar\rho_2(E_0+E^+)Z}, \quad (2.33)$$

where, to avoid excessive complication, the contribution of adiabatic degrees of freedom has been ignored¶ and $\chi = 1$ has been assumed.

We cannot write an explicit expression for $k(T)$ using the stepwise excitation mechanism in the transition region, because the non-equilibrium distribution function must be determined by solving a system of related equations or from the Fokker–Planck equation. A few results have been obtained for relatively simple models discussed by Nikitin[16].

3. RECOMBINATION

The rate of recombination—the reverse process to dissociation—can be calculated in terms of the rate of dissociation and the thermodynamic equilibrium constant. In spite of the fact that both dissociation and recombination produce a disturbance of the equilibrium distribution, there are conditions under which the following relation holds true:

$$k_d/k_r = K_{eq}\ . \quad (3.1)$$

We shall not discuss them here: the reader is referred to the literature[17-26]. We shall only point out that two limiting regions of pressure exist also for recombination, corresponding to third-order and second-order kinetics respectively, as well as a transition region of pressures. Since the following equality applies

$$K_{eq} = F_AF_B/F_{AB}\exp(-D/kT)\ , \quad (3.2)$$

the recombination constant can be written, in terms of the factor $A(T)$ which characterises the rate of decomposition, in the form

$$k_r = A(T)\frac{F_{AB}}{F_AF_B}\ . \quad (3.3)$$

We shall discuss this expression in greater detail for the case of recombination of atoms. Using the fact that $Z \simeq T^{1/2}$ and $F_AF_B \simeq T^3f_A^{el}f_B^{el}$, we arrive at the following expression for the temperature dependence of k_r:

$$k_r \simeq Zg_{el}g_{rot}\ \frac{\Delta E^*}{kT} = \frac{T^{3/2}T}{T^3f_A^{el}\ f_B^{el}}\,g_{el}\,g_{rot}\ \frac{\Delta E^*}{kT}\ . \quad (3.4)$$

Eqn. (3.4) assumes the single-quantum transition model, whereas Eqn. (3.5) is based on the diffusion model ignoring the temperature dependence of f_A^{el} and f_B^{el}:

$$k_r \simeq Zg_{el}g_{rot}\ \frac{\langle\Delta E^2\rangle}{2(kT)^2}\rho(E_0-kT)\frac{T^{3/2}T^2}{T^3f_A^{el}f_B^{el}} \simeq g_{el}\,g_{rot}\ \frac{\langle\Delta E^2\rangle}{kT}\rho(E_0-kT) \quad (3.5)$$

In many instances, however, the electronic part of the partition functions of atoms is a sensitive function of temperature because of the contribution from the lower excited states, and this must of course be taken into consideration when calculating the temperature dependence of the constant k_r by formula (3.3).

¶ The influence of adiabatic degrees of freedom, which is relatively small for polyatomic molecules, has been considered in the work of Marcus[15].

If the molecule is described approximately by means of a Morse oscillator, the quantity ΔE^* is evaluated by the Massey criterion (2.26), and account is taken of the temperature dependence of g_{el}, the following equation can be derived from Eqns. (3.4) and (3.5):

$$k_r \simeq g_{rot}\ (T)\frac{\Delta E^*}{kT} \simeq T^{-m-1/2},\ m \simeq 1/2 \text{ to } 1/3. \quad (3.6)$$

Thus, the theory predicts a negative temperature coefficicient for the rate constant of recombination. However, the following restrictions must be borne in mind.

Firstly, Eqns. (3.4), (3.5), and (3.6) have been derived on the assumption that the third body M is an inert gas atom. If internal degrees of freedom in M can play a significant role in the deactivation of the excited AB pair, the temperature dependence of the constant k_r may be different from Eqn. (3.6). We may assume that the main difference will be that here the quantity ΔE^* is not given by formula (2.26).

Secondly, the possibility of recombination through the formation of an intermediate complex has been ignored in the derivation of Eqns. (3.4) and (3.5):

$$A + M \rightarrow AM \quad (3.7a)$$

$$AM + B \rightarrow AB + M\ . \quad (3.7b)$$

In this recombination mechanism the constant k_r must contain the exponential term $\exp(\epsilon/kT)$, arising essentially because the recombination reaction involves bound AM pairs with a bond energy ϵ. The value of ϵ varies between 0.5 and 5 kcal mole^{-1} for different molecules†. Hence expressions of the type of (3.6) are applicable only at relatively high temperatures, when $\epsilon/kT \ll 1$.

Lastly, we should note that when recombination occurs under conditions such that three-body A + A + A collisions are significant, the temperature dependence of the recombination constant may be noticeably affected by the exchange reaction[27]

$$A_2 + A \rightarrow A + A_2\ . \quad (3.8)$$

Direct experimental evidence exists that the reaction (3.8) is important in the vibrational relaxation of diatomic molecules even at low levels[28]. Since the rate of reaction (3.8) must increase as the vibrational energy of the A_2 molecule increases, it is reasonable to expect that reaction (3.8) can provide an effective means of removing energy from the latterly formed A_2 molecule in the vibrational deactivation of the higher states.

The recombination of oxygen in an argon atmosphere[29] is one of the few examples of recombination processes for which the temperature dependence of the rate constant has been definitely characterised.

4. EXCHANGE

Exchange reactions, like dissociation and recombination, can give rise to varying degrees of disturbance of the equilibrium distribution. However, unlike the other reactions, the exchange reaction does not usually show a change in reaction order due to disturbance of the equilibrium distribution. This is because both the relaxation and particularly the redistribution of atoms occur during collisions of molecules of the same type. Perturbation of the equilibrium distribution will change the order of the reaction

† This mechanism was studied in detail by Rice[26].

with respect to the concentration of the reacting molecules only if conditions are such that relaxation and exchange occur as a result of collisions between different molecules. We shall deal later with one example of a process of this type, but first we must discuss the calculation of $k_{ex}(T)$ within the bounds of equilibrium theory. This approximation is known to be realistic for exchange reactions occurring in a dense atmosphere of inert gas, which ensures sufficiently fast relaxation.

Starting with the basic formula of the transition state method, we shall consider processes involving three or four atoms. Take the simplest exchange process, of the type

$$A + BC \rightarrow AB + C \ . \qquad (4.1)$$

We note that the critical surfaces S^+ are chosen in different ways according to whether or not the reaction involves an activation energy. For surfaces with a potential barrier the reaction coordinate is most naturally identified as the line of fastest descent from the saddle point. We assume that rotation can be separated from vibration and from motion along the reaction coordinate, both in the starting systems and in the activated complex. Then the general formula of the transition state method can be written in detail as follows:

$$k_{ex} = \frac{kT}{2\pi\hbar}\varkappa g^+ \frac{F^+_{AB}}{F_A F_B}\exp(-E_a/kT) =$$

$$= \frac{kT}{2\pi\hbar}\varkappa g^+ \frac{(F^+_{AB})_{tr}\,(F^+_{AB})_{vibr}(F^+_{AB})_{rot}}{(F_AF_B)_{tr}\,(F_AF_B)_{vibr}(F_AF_B)_{rot}}\exp(-E_a/kT) \ . \quad 4.2)$$

Having thus adopted a concrete model for S^+, we find that the partition function F^+ in the general formula (4.2) acquires a definite meaning: $(F^+_{AB})_{rot}$ is calculated as the partition function of a solid with atoms fixed at the points q^+_i, and $(F^+_{AB})_{vibr}$ as the partition function of a system of harmonic oscillators with normal frequencies ω^+_i, referred to the non-rotating system of atoms with a fixed value of the reaction coordinate q^+_r.

For a reaction involving three atoms, the expression for k_{ex} takes different forms for linear and triangular complexes. In the former we have three vibrational and two rotational degrees of freedom; In the latter, two vibrational and three rotational. The temperature dependence of k is as follows:

linear complex

$$k_{ex} \simeq T^{1/2}\frac{(1-e^{-\hbar\omega_{BC}/kT})}{\prod_{i=1}^{2}(1-e^{-\hbar\omega^+_i/kT})}\exp(-E_a/kT) =$$

$$= \begin{cases} T^{-1/2}\exp(-E_a/kT), & \hbar\omega_i/kT \gg 1 \qquad (4.3a) \\ T^{3/2}\exp(-E_a/kT), & \hbar\omega_i/kT \ll 1\ ; \qquad (4.3b) \end{cases}$$

triangular complex

$$k_{ex} \sim \frac{(1-e^{-\hbar\omega_{BC}/kT})}{\prod_{i=1}^{3}(1-e^{-\hbar\omega^+_i/kT})}\exp(-E_a/kT) = \begin{cases} \exp(-E_a/kT), & \hbar\omega_i/kT \gg 1 \ (4.4a) \\ T\exp(-E_a/kT), & \hbar\omega_i/kT \ll 1 \ (4.4b) \end{cases}$$

We can follow the transition between these two examples by taking account of the interaction between vibrations and rotation in the calculation of F^+, and by abandoning the "rigid rotator–harmonic oscillator" model used for computing the spectroscopic approximation. The rate constant expressed in the form of (4.4) is applicable only to a complex ABC^+ in which the angular departure from the linear configuration is significantly larger than the angular amplitude of the bending vibrations. As regards the temperature dependence of the pre-exponential term in (4.3) and (4.4) we note that at low temperatures the indicated dependence will apply only as long as the tunnel corrections can be ignored. The limitation at high temperatures arises from the condition that the mean vibration amplitude must be small as compared with the effective width of the potential well $1/\alpha$‡. This limitation can be expressed as a requirement that the value of the full pre-exponential factor must be substantially less than the number of collisions given by gas kinetics. If the relationship

$$\frac{kT}{2\pi\hbar}\frac{F^+_{ABC}}{F_A F_{BC}} < Z_{A-BC} \ , \qquad (4.5)$$

were formally found not to be obeyed, we would need to use as pre-exponential term the factor Z_{A-BC}, which gives a $T^{1/2}$ temperature dependence[30] to the pre-exponential term instead of $T^{3/2}$ as in (4.3) or T as in (4.4).

We shall now consider the potential energy surface in the absence of an activation barrier. The situation is typical of ion–molecule reactions, and can also arise in the reaction of various atoms with molecules.

If the interaction between the species A and BC at large enough distances corresponds to attraction, the reaction rate is in many instances determined by the rate of formation of the long-lived ABC* complex. In practice, of course, the complex ABC* can decompose either in the direction of AB + C or in the direction of A + BC, but conditions are often met when decomposition in the reverse direction can be ignored. With these assumptions, reaction (4.1) can be described by the following model: if the radial velocity of the approaching particles is sufficient to overcome the centrifugal barrier, the complex ABC* is formed, and then decomposes into the molecules AB + C. If the interaction potential is centro-symmetrical the model is described by a critical surface S^+ coinciding with a sphere of radius R_m corresponding to the coordinate of the centrifugal barrier.

Such an S^+ surface is determined not only by the characteristics of the potential, but also by the integrals describing the motion of the system under study, since R_m depends on the angular momentum of the relative motion of A and BC.

Calculations of this type[31] for potentials $U(R) \simeq R^{-s}$, with $s = 4$ (polarisation interaction) and $s = 6$ (van der Waals interaction) lead to the following expressions for the rate constants

$$k_{ex} = 2\pi e\,(\alpha/\mu)^{1/2} \ , \qquad (4.6)$$

$$k_{ex} = 2^{3/2}\,3^{1/2}\,\Gamma(2/3)\frac{\pi^{1/2}}{\sigma^+}(kT)^{1/6}\left[\frac{\alpha_1\alpha_2 I_1 I_2}{I_1+I_2}\right]^{1/2}\mu^{-1/2} \ . \qquad (4.7)$$

Here α denotes the polarisability of the neutral partner in an ion–molecule reaction characterised by the polarisation potential $U(R) = -e^2\alpha/2R^4$; α_1 and α_2 are the polarisabilities of the neutral partners, for which the long-range component of the potential can be approximated by the expression involving the ionisation potentials I_1 and I_2 of the partners $U(R) = \frac{1}{2}\frac{\alpha_1\alpha_2}{R^6}\frac{I_1 I_2}{I_1+I_2}$. It is important to note that the partition functions for the internal motion of the partners do not appear in (4.6) and (4.7). This is

‡ This limitation allows us to separate rotation from vibrations, and also to treat vibrations by the harmonic approximation.

simply because with the critical surface S^+ assumed here the reaction (that is, the intersection of S^+) occurs at such large distances that the contributions of internal motions to F and F^+ can be taken to be identical and drop out of the ratio F^+/F.

It is permissible to ignore the short-range part of the potential in the calculation of R_m only if R_m is much greater than the gas-kinetic cross-section R_0. This sets a high-temperature limit to the validity of expressions (4.6) and (4.7): the condition

$$k_{ex} > Z_0 . \qquad (4.8)$$

which states that only the long-range part of the potential contributes to the rate constant, must apply.

We shall now discuss the way in which formulae (4.3) and (4.4) are related to the expression (1.1).

If we describe the rate constant of our exchange process by the Arrhenius formula (1.1) with a constant factor, and if we express the exponential functions of temperature for the low- and the high-temperature regions in the form

$$T^n = (e\bar{T}_l)^n \exp(-nkT_l/kT), \qquad (4.9a)$$

and

$$T^m = (e\bar{T}_h)^m \exp(-mkT_h/kT), \qquad (4.9b)$$

where $\bar{T}_l$ and $\bar{T}_h$ denote some mean temperature in the low- and in the high-temperature region respectively, we obtain

$$E_l = E_0 + nk\bar{T}_l, E_h = E_0 + mk\bar{T}_h. \qquad (4.10)$$

Hence,

$$\Delta E = E_h - E_l = k(m\bar{T}_h - n\bar{T}_l) . \qquad (4.11)$$

Since, according to formulae (4.3) and (4.4), we have $n = -\frac{1}{2}$ and $m = \frac{3}{2}$ for a linear complex and $n = 0$ and $m = 1$ for a triangular complex, in the former instance expression (4.11) takes the form

$$\Delta E = \frac{k}{2}(3\bar{T}_h - \bar{T}_l) \qquad (4.12a)$$

and in the latter

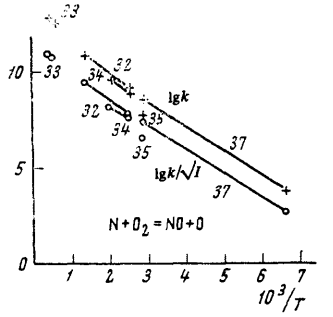
$$\Delta E = k\bar{T}_h . \qquad (4.12b)$$

We see that in both the quantity ΔE is greater than 0, that is, $E_h > E_l$. Thus, the activated complex theory requires that the activation energy should not remain constant on going from low to high temperatures but should increase with increase of temperature if the rate constant of an exchange process is described by the Arrhenius law (1.1).

The following example confirms the conclusions of the theory. One of the constants for which the numerical values obtained by different workers show the most satisfactory agreement is the rate constant of the reaction

$$N + O_2 \rightarrow NO + O + 32\ \text{kcal mole}^{-1}. \qquad (4.13)$$

Data obtained by the formulae proposed by different authors [32-37] for the appropriate temperature ranges are graphically compared in the Figure, where the quantities $\lg k_{ex}$ or $\lg[k_{ex}/\sqrt{T}]$ are plotted as ordinate and $10^3/T$ is the abscissa. It is evident from the Figure that neither $\lg k_{ex}$ nor $\lg[k_{ex}/\sqrt{T}]$ is a linear function of $1/T$. It follows that formulae (1.1) and (1.2) do not adequately describe this constant over the whole of the experimental temperature range (145-3300°K). It can also be seen from the Figure that, as the above theory requires, the effective activation energy increases with increase of temperature.



Temperature dependence of the rate constant of the reaction $N + O_2 \rightarrow NO + O$. The numbers by the points are literature references.

The following considerations also militate against the description of the rate constant of an exchange reaction by a formula of type (1.1) or (1.2) over a wide temperature range. The temperature dependence of the equilibrium constant of the reaction A + BC = AB + C is given by the expression

$$K_{eq} \simeq \frac{1-\exp(-\hbar\omega_{BC}/kT)}{1-\exp(-\hbar\omega_{AB}/kT)} \exp(-Q_0/kT). \qquad (4.14)$$

Since the equilibrium constant is the ratio of the rate constants for the forward and the reverse reaction, expressing these constants by Arrhenius formulae of the type (1.1) or (1.2) gives

$$K_{eq} = \frac{A}{A'} \exp[-(E_0 - E_0')/kT)] = \frac{A}{A'} \exp(-Q_0/kT)], \qquad (4.15a)$$

$$K_{eq} = \frac{A_0\sqrt{T}}{A_0'\sqrt{T}} \exp[-(E_0 - E_0')/kT) = \frac{A_0}{A_0'} \exp(-Q_0/kT). \qquad (4.15b)$$

Comparing these formulae with (4.10) we see that A and A' (or A_0 and A_0') can be treated as constant and temperature-independent only when $\omega_{BC} = \omega_{AB}$. Thus, if, for example, $\omega_{AB} = 2\omega_{BC}$, the quantity

$$[1 - \exp(-\hbar\omega_{BC}/kT]/[1 - \exp(-\hbar\omega_{AB}/kT)]$$

and therefore also the ratio A/A' or A_0/A_0', will decrease by a factor of two on going from the low-temperature to the high-temperature region.

The ratio of the pre-exponential factors should be even more clearly a function of temperature for an exchange reaction of the type

$$AB + CD \rightarrow ABC + D . \qquad (4.16)$$

The temperature dependence of the equilibrium constant, making the same assumptions as in (4.1), should now be given by the expression

$$k_{ex} \simeq T^{-1/2} \frac{(1-e^{-\hbar\omega_{AB}/kT})(1-e^{-\hbar\omega_{CD}/kT})}{\prod_{i=1}^{3}[1-\exp(-\hbar\omega_{ABC}^i/kT)]} \exp(-Q_0/kT). \qquad (4.17)$$

In the low-temperature region this leads to

$$k_{ex} \simeq T^{-1/2} \exp(-Q_0/kT) , \qquad (4.18)$$

and in the high-temperature region

$$k_{ex} \simeq T^{1/2} \exp(-Q_0/kT). \qquad (4.19)$$

The basic postulate of the transition state method, concerning the possibility of introducing a single reaction coordinate, cannot be tested by comparing theory with experiment because, on the one hand, the characteristics of the potential energy surface are not usually known, and on the other hand the degree of perturbation of the equilibrium distribution is not known. Therefore it is particularly interesting to compare the values of $k_{ex}(T)$ calculated for the same model by the transition state method and by averaging the occurrence of the reaction over the equilibrium distribution function. Calculation of σ is possible only with the help of fast computers, and only within the limits of classical mechanics for the present. Such a comparison made by Karplus and coworkers [38] for the reaction H + H_2, does not allow us to assess unequivocally the precision of the transition state method, but it provides evidence that no serious error is introduced into the temperature dependence of the rate constant $k_{ex}(T)$ by using this method. Similar investigations were recently carried out by Marcus [39,40].

Thus, it is at least possible that the transition state method will provide an acceptable estimate of the temperature dependence of $k(T)$ provided that the reaction does not significantly disturb the equilibrium distribution. It is essential, of course, to take account of the temperature dependence of the transmission coefficient for non-adiabatic reactions and reactions with light atoms, as in formulae (2.3)-(2.7).

Theoretical attempts to explain the influence of perturbation of the equilibrium distribution on the rate of an exchange reaction have concentrated not so much on calculating the non-equilibrium rate constant as on defining the conditions under which the effect is small [41-44]. It was assumed that the cross-section of the reaction depends on the relative kinetic energy, but no attempt was made to derive a concrete expression. Since the Maxwell distribution is re-established in a very short time—after a few collisions—an exchange reaction involving a sufficiently high activation energy cannot significantly affect the equilibrium distribution of velocities. This ceases to be true when the main contribution to overcoming the energy barrier is provided by the vibrational energy of the partners. We cannot exclude the situation in which the rate of vibrational relaxation is comparable with or even smaller than the rate of reaction calculated on the assumption that the Boltzmann distribution in the vibrational states is preserved. Then the true rate of the exchange reaction will be determined only by the rate of vibrational relaxation, or rather by the rate at which the reacting molecules reach the particular vibrational level which makes the largest contribution to the cross-section of the reaction. In this sense we have complete analogy with unimolecular reactions, for which the rate of decomposition at low pressures is determined by the rate of vibrational excitation of the molecules. Since the temperature dependence of the vibrational relaxation time is described not by the Arrhenius formula (1.1) but by the Landau-Teller formula [4]

$$k_{vibr} \sim \exp[-(T_0/T)^{1/3}], \qquad (4.20)$$

it may happen that the rate of an exchange reaction also will not contain an Arrhenius factor. No definite statements regarding the particular degrees of freedom which contribute most significantly to the cross-sections of various exchange reactions can as yet be made.

The study [38] of the H + H_2 → H_2 + H reaction, already mentioned, showed that the main contribution to overcoming the activation barrier comes from kinetic energy. This points to a relatively insignificant disturbance of the equilibrium distribution by the reaction. On the other hand, in a reaction of the type $H_2 + D_2 \rightarrow HD + HD$ the main contribution may come from the vibrational energy of the partners, since the decomposition of the $[H_2D_2]$ complex into two HD fragments is caused by vibrations. In this example a substantial disturbance of the equilibrium distribution can be expected. A recent investigation by Bauer and coworkers [45,46] has shown that the kinetics of this reaction do not obey a second-order law, and that the rate depends on the concentration of argon (used only as a thermal reservoir to ensure vibrational relaxation of H_2 and D_2). This change in reaction order is evidence of a disturbance in the equilibrium distribution§, and therefore that the transition state method is not applicable to the calculation of $k_{ex}(T)$. Unfortunately, no alternative method of calculating the rate constant can be suggested at present.

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CHEMICAL REACTIONS OF DIENE POLYMERS

I.A.Tutorskii, S.V.Novikov,
and B.A.Dogadkin

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I. INTRODUCTION

Diene polymers are now the most widely used of all known polymeric materials. The polymerisation of dienes leads to the production of elastomers which acquire all the necessary properties during further treatment (plasticising, vulcanising). In addition to the problem of the processing and modification there is the problem of stabilising the polymer material. The effective solution of these problems is impossible without a knowledge of the chemical nature of the polymers used.

It is necessary to point out that there has not yet been any detailed investigation of the reactivity of diene polymers as a class of organic compounds. Most of the studies in the field of the chemistry of diene polymers are of an applied nature and are connected with the study of the vulcanisation and stabilisation of polymers or are directed to the study of individual reactions of diene polymers, such as chlorination, hydrochlorination, etc. At the same time, without knowing the general features of the chemistry of diene polymers it is impossible to carry out effectively work of an applied character, directed to the solution of particular practical problems.

The present review aims to be a critical consideration and systematisation of the published information on the chemistry of diene polymers up to the end of 1965. An attempt has been made to find the characteristics of the double bonds in polymers having a regular 1,5-polyene structure. The review does not attempt a detailed examination of the information on vulcanisation and oxidation that has appeared in monographs.

II. ADDITION TO A DOUBLE BOND

1. Reaction with Compounds Containing a Mercapto-Group

The reactions of hydrogen sulphide and thiols with alkenes have been studied in detail by Naylor[1]. Under the catalytic action of sulphur, hydrogen sulphide is readily added at the double bond of polyisoprene in accordance with the Markovnikov rule. The thiol formed can react with another double bond to give a sulphide. The oxidation of two thiols leads to the formation of a disulphide. As a result of the last two reactions, cross-linking of the macromolecules of the rubber takes place. In the presence of a peroxide or on ultraviolet irradiation, hydrogen sulphide adds at the double bond of polyisoprene contrary to the Markovnikov rule.

The addition of alkyl and aryl thiols to a double bond also proceeds in accordance with the Markovnikov rule in the presence of sulphur and contrary to the rule when the reaction is carried out in the presence of peroxide[2]. The easier it is for homolytic rupture of the S–H bond, the greater the acidity of the thiol, and the more active the thiol relative to the double bond. Prilezhaeva and Shostakovskii[3] give the following series for the activity of thiols in relation to alkenes:

$$C_6H_5SH > HOOC.CH_2SH > RCH_2SH > R_2CHSH > R_3C.SH.$$

Electron-donating groups in the thiyl [mercapto-] radical reduce its reactivity towards double bonds; electron-withdrawing groups, on the other hand, increase its activity. A drop in the electron density of the double bond leads to a decrease in its reactivity towards thiols.

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II. ADDITION TO A DOUBLE BOND

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Electron-donating groups in the thiyl [mercapto-] radical reduce its reactivity towards double bonds; electron-withdrawing groups, on the other hand, increase its activity. A drop in the electron density of the double bond leads to a decrease in its reactivity towards thiols.

Conjugated, vinyl, terminal double bonds, and also double bonds in rings react readily with thiols, but inner non-conjugated double bonds are less reactive towards thiols[4].

Natural rubber exhibits a low reactivity towards thiols. It does not react with ethyl thiol, isopentyl thiol, thiophenol[5], or tri- and hexa-methylenedithiols[6] when the reaction is performed in an inert medium in the presence of peroxide or under ultraviolet irradiation. At the same time the addition of thiols to low-molecular-weight alkenes, which model the structure of polyisoprene, does take place under analogous conditions. Cunneen found the following series for the activity of alkenes in relation to thiols: cyclohexene > dihydromyrcene > squalene > natural *cis*-polyisoprene.

The addition of thiols to the double bonds of diene polymers takes place when atmospheric oxygen participates in the reaction as a third component or when the reaction is carried out in latex. Hull and coworkers[7] vulcanised natural rubber on rollers in air with the aid of aliphatic and aromatic dithiols, inert relative to polyisoprene when the reaction is carried out in a solvent in the absence of atmospheric oxygen. Foxly[8] notes the reactivity of dodecanethiol towards polyisoprene when the reaction is performed in solution in the presence of oxygen, whereas in an inert medium these substances do not react. Dogadkin and coworkers[9] observed the reaction of thiols with polyisoprene in the presence of oxygen and the absence of reaction between them in an inert medium, even at elevated temperatures. Pierson and coworkers[10] achieved a high saturation of polybutadiene with methanethiol by carrying out the reaction in latex with an excess of the thiol at 30–60°C in the presence of azoisobutyronitrile. Serniuk and coworkers[4] described the reaction of ethanethiol with diene polymers in latex.

The reaction of thioglycollic acid and its derivatives with diene polymers has received considerable attention. It was found that when the reaction of natural polyisoprene with thioglycollic acid[5] and its esters[11,12] was carried out in an inert medium, over a wide range of temperatures, in the presence of initiators (azoisobutyronitrile, cumene hydroperoxide), and with ultraviolet irradiation, addition of the above thiols at the double bond did not occur. Nevertheless thioglycollic acid adds readily to cyclohexene, 1-methylcyclohexene, and dihydromyrcene in the presence of peroxides at room temperature, and to squalene under ultraviolet irradiation[5]. Ethyl thioglycollate adds to isopentene to 67% extent and to dihydromyrcene to 30%, but does not react with natural *cis*- and *trans*-polyisoprenes under the same conditions[11,12].

Such difference in the reactivity of the polyisoprenes and model low-molecular-weight compounds to relatively weak electrophilic agents is explained by the mutual influence of the double bonds in the 1,5-polyene systems, leading to a decrease in their electron density[13].

From the standpoint of classical chemistry, the possibility of the mutual influence of double bonds through two C–C bonds, and especially through three, is inadmissable. However, the experimental results show that a methylene bridge is not a serious impediment or high barrier for the conjugation of a chain[14]. As Voevodskii and coworkers found by the EPR method[15,16], this interaction of double bonds is also possible where there is an ethylene bridge. The establishment of the mutual interaction of double bonds through one C–C bond is accompanied by considerable drop in the energy of the molecule (5–50 kcal mole^{-1}). For the 1,5-diene this interaction energy is appreciably less, but nevertheless sufficient to show the significant influence of the double bonds on reactivity[15]. On going from a 1,5-diene to a 1,5-polyene system the energy of the mutual influence of double bonds increases, which appears as the observable drop in reactivity.

The inertness of the polyisoprenes to thioglycollic acid and its esters does not appear when atmospheric oxygen[17,18] participates in the reaction as a third component or when the reaction is effected in latex[4,19]. In the latter instance the reaction is apparently catalysed by the substances of the non-rubber part of the latex globules. The mechanism of this catalysis has not been discussed in the literature.

Cunneen[20] studied the reaction of thioacetic acid and its chloro-derivatives with natural *cis*-polyisoprene and with model compounds. Thioacetic acid adds quantitatively to polyisoprene in benzene on ultraviolet irradiation for several hours. In the absence of radiation the reaction does not occur even at 100–130°C. Monochlorothioacetic acid adds quantitatively to polyisoprene in the dark in the presence of ascaridole. Ultraviolet radiation accelerates the reaction. The reaction of polyisoprene with di- and trichlorothioacetic acids takes place similarly.

A comparison of the reactivity of double bonds in polyisoprene, cyclohexene, dihydromyrcene, and squalene towards thioacetic acids showed that the order of activity of these alkenes is as found for reaction with thiols.

Ritter[21,22] gives the following series for the activity of thio-acids towards natural *cis*-polyisoprene: thiocaprylic > > thiobenzoic > thio-2-naphthoic > thioacetic > thiostearic > trichlorothioacetic acid. The reaction was effected in xylene (6% solution of the polymer) in two stages. In the first stage a slight excess of the thio-acid was introduced, and the reaction was carried out at room temperature in carbon dioxide atmosphere, in the light for a week. In the second stage the product reacted with a 25% excess of the thio-acid for 8 days at room temperature in the light, in carbon dioxide atmosphere. The finding that thioacetic acid is more reactive than trichlorothioacetic contradicts Cunneen's results[20] and seems doubtful to us.

Dithioadipic and dithiosebacic acids[6] add to natural *cis*-polyisoprene on rolling, leading to cross linking of the macromolecules. Peroxides and ultraviolet irradiation accelerate the reaction. The reaction of dithioadipic acid with polyisoprene in benzene (10% solution of the polymer) reaches 45% at 100°C.

The dithio-acids obtained as a result of the replacement of both oxygen atoms of the carboxyl group by sulphur do not add to natural *cis*-polyisoprene[21].

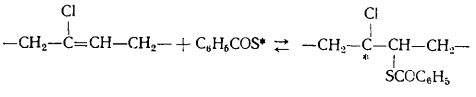
The reaction of thiobenzoic acid with natural *cis*- and *trans*-polyisoprenes has been investigated in detail[11,12,23]. The reaction was effected in an inert medium (argon), in xylene and chlorobenzene, over a wide range of temperatures (20–125°C) and concentration range 0.05–1.0%. The polymer and thio-acid were taken in an equimolecular ratio with cumene hydroperoxide as initiator of the reaction. The reaction proceeds by a radical mechanism, and the extent of the reaction is proportional to the amount of initiator; the temperature dependence has a maximum at about 60–80°C. There is an anomalous dependence of the extent of reaction on the concentrations of the reactants, with a maximum at 0.1–0.3%, this being connected with the

association of macromolecules of polyisoprene in this concentration region. A significant difference in reactivity between *cis*- and *trans*-polyisoprenes to thiobenzoic acid was not observed.

The amount of thiobenzoic acid in the high-molecular-weight fraction of the reaction products greatly exceeds the mean consumption of the thio-acid in the reaction, which is possible only under the non-statistical occurrence of the reaction of polyisoprenes with thiobenzoic acid. The non-statistical nature of the addition of thiobenzoic acid to polyisoprenes is the result of the development of a reaction by an intramolecular chain mechanism. As noted above, in 1,5-polyene systems there is interaction of the double bonds, leading to a drop in their reactivity. The addition of molecules of the thio-acid at one double bond in such a system leads to an increase in the electron density at two neighbouring double bonds owing to the breakdown of the conditions for their interaction. Hence a single act of addition leads to the activation of two double bonds. The probability of addition of subsequent molecules of thio-acid at such double bonds increases, and subsequently the addition of thiobenzoic acid takes place selectively, that is, it is not a random double bond that reacts, but a double bond in the vicinity of the one that has already reacted. The disappearance of an activated double bond during the reaction in turn leads to the activation of a new double bond. Conditions are created for the development of a chain intramolecular mechanism of reactions of 1,5-polyene systems.

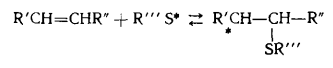
An investigation of the reaction of polychloroprene with thiobenzoic acid[24] showed the influence of the strongly electronegative atom of chlorine located at the double bond, on the reactivity of double bonds regularly alternating in the 1,5 positions. Whereas the addition of thiobenzoic acid to polyisoprenes takes place by a radical mechanism, with polychloroprene this mechanism is not realised. The introduction of up to 12 mole % cumene hydroperoxide into the reaction mixture has no effect on the rate or extent of reaction.

Evidently the macroradical which is formed as a result of the addition of a thioyl radical at a double bond:



is considerably stabilised by the action of the electronegative chlorine atom and is incapable of continuing the reaction chain. An ionic mechanism for the reaction is also excluded, since the dielectric constant of the solvent, when varied within wide limits, has no influence on the rate or extent of the reaction. It was suggested that the addition of thiobenzoic acid at the double bond of polychloroprene takes place with the formation of an intermediate molecular complex.

Sivertz and coworkers' kinetic studies[25-28] showed the addition of a thiyl radical at a double bond to be highly reversible when the reaction took place in the gas or liquid phase:



As a result of the decomposition of the intermediate complex the double bond is regenerated in either the *cis*- or the *trans*-configuration. In the reaction of methanethiol with but-2-ene the rate of decomposition of the intermediate complex to form *trans*-butene is four times that to form the *cis*-butene and 80 times the rate of formation of the addition product. The high reversibility of the addition of thio-compounds at double bonds is responsible for the isomerisation of the double bonds in such reactions.

Cunneen and Shipley[29] observed the isomerisation of natural *cis*-polyisoprene during its reaction with thio-acids. Small quantities (0.1–1.0%) of chlorothioacetic, trichlorothioacetic, and thionaphthoic acids were used. The reaction was carried out in solution and in latex, under vacuum, without a catalyst, for 6 h at 100°C. Thionaphthoic acid was the most effective.

The isomerisation of the natural *cis*- and *trans*-polyisoprenes in their reaction with thiobenzoic acid was studied on rollers, in solution, and in latex[30,31]. The equilibrium ratio of *cis*- and *trans*-structures in the isomerised products was found to be 43 : 57. The high efficiency of the isomerising agent is noted—a considerable degree of isomerisation is obtained when the system has one molecule of thiobenzoic acid per 1270 isoprene links. Monochlorothioacetic, trichlorothioacetic, thionaphthoic, thiosalicylic, and thiostearic acids had similar effectiveness as isomerisation agents[32].

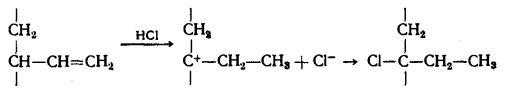
Results on the isomerisation of *cis*-polybutadiene in the presence of thio-compounds are somewhat contradictory. Golub[33] and Seely[34] consider that in equilibrium isomerisation the *cis*- and *trans*-isomers reach a ratio of 5 : 95. Berger and Buckley[35], on carrying out the isomerisation of *cis*- and *trans*-polybutadiene after Golub, found the equilibrium ratio of the *cis*- and *trans*-structures to be 25 : 75. The isomerisation was performed in solution at 25°C, with benzene and toluene as solvents. The isomerisation agents were thionaphthoic acid and diphenyl sulphide, the reaction was carried out under ultraviolet irradiation. The rate of isomerisation increased with the polymer concentration and with the intensity of the radiation; it was independent of concentration of the isomerising agent in the range 1–10 g litre^{-1}.

2. Reactions with Hydrogen Halides

The reaction of natural *cis*-polyisoprene with hydrogen fluoride was described by Tom[36]. The reaction was carried out in solution at temperatures between −26° and +40°C. In the addition of hydrogen fluoride to the double bonds considerable cyclisation is observed, brought about by the back reaction which eliminates HF, and with rise in temperature the rate of cyclisation increases. At 40°C, there is no addition, only cyclisation. The final product always contains some unreacted double bonds. The best solvent for the addition is xylene; there is considerable cyclisation in benzene and toluene; addition does not take place in carbon tetrachloride and chloroform. In xylene at −26°C the hydrogen fluoride added is 70% of that theoretically possible, and 25% of the double bonds participate in the cyclisation. The temperature and time dependences of the extent of the addition reaction are curves with a maximum.

The reaction of diene polymers with hydrogen chloride has received considerable attention. Hydrogen chloride adds readily to natural *cis*-polyisoprene at moderate temperatures in the bulk, in solution, and in latex[37]. In the presence of peroxide the addition proceeds by a radical mechanism contrary to the Markovnikov rule[38,39]. Synthetic polyisoprene[37] gives a product with incomplete addition. The methylated double bonds in polyisoprene are more reactive than the double bonds of polybutadiene.

As a result of the addition of hydrogen chloride to polyisoprene a tertiary chloride is formed. The vinyl bonds in polybutadiene can also form a tertiary chloride thanks to the Whitmore rearrangement:



Staudinger[40] found a considerable decrease in the viscosity of solutions of natural *cis*- and *trans*-polyisoprenes during hydrochlorination and showed that this is the result of cyclisation taking place simultaneously with addition.

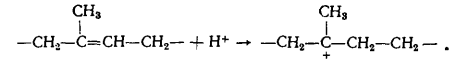
The formation of intramolecular rings during hydrochlorination of natural rubber was also observed by Gehman[41]. Later investigations were quite contradictory and indicated that either there is complete cyclisation during hydrochlorination with subsequent ring opening under the action of HCl[42] or the reaction is restricted to addition and *cis*–*trans*-isomerisation, and cyclisation does not take place at all[43,44]. This conclusion was reached by the authors from calculations of the balance of the double bonds in the reaction products. The sum of the remaining double bonds and the bonds which had disappeared as a result of the addition of chlorine is equal to the degree of unsaturation of the original polymer. Golub and Heller[45] showed, with the aid of high-resolution NMR, that hydrochlorination of natural rubber and balata is accompanied by cyclisation, whereas *cis*–*trans*-isomerisation takes place to a negligible extent or does not occur at all.

In the reaction of 3,4-polyisoprene with hydrogen chloride[46] a predominantly monocyclic structure is formed, with the addition of one molecule of HCl to two double bonds. The cyclohydrochlorination of 3,4-polyisoprene proceeds by an ionic mechanism. Support for the formation of a monocyclic structure is provided by the proportion of chlorine in the reaction products and also by the results of NMR and infrared spectroscopy.

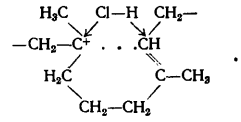
Whereas the cyclohydrochlorination of 3,4-polyisoprene takes place at 10–80°C, the analogous reaction for 1,2-polybutadiene requires much more severe conditions. The product of the cyclohydrochlorination of 1,2-polybutadiene also has a monocyclic structure.

van Veersen[47] investigated the influence of solvents on the hydrochlorination of natural *cis*-polyisoprene. When the reaction takes place in toluene the kinetic curves are smooth. In a mixture of toluene with ethyl acetate or dioxan, the reaction shows a definite induction period. The appearance of an induction period was associated by van Veersen with the reaction proceeding through the intermediate stage of the formation of a π-complex. Competition by oxygen-containing solvents, which can also form π-complexes with hydrogen chloride, also leads to the appearance of the observed induction period for the reaction. The negative temperature coefficient of the reaction is also considered as proof that the reaction proceeds through the formation of a π-complex[47,48].

Gordon and Taylor[49] assume that the addition of hydrogen chloride to *cis*-polyisoprene proceeds via the formation of an intermediate carbonium ion, as occurs in the cyclisation. In accordance with the suggested scheme of reaction a proton is added at the double bond to form a carbonium ion:



The latter forms a pseudocyclocarbonium ion:



Next a neutral molecule of hydrogen chloride is added at the pseudobond. The latter act leads to the regeneration of the carbonium ion. In accordance with this scheme the addition of neutral molecules of hydrogen chloride at the double bonds of polyisoprene, which alternate regularly in the 1,5-position, should proceed by an intramolecular chain mechanism. The high rate of hydrochlorination is considered by the authors to be one of the arguments supporting an intramolecular chain mechanism for the addition of hydrogen chloride to polyisoprene. In this they do not admit the possibility of electronic interaction of double bonds separated by three C–C bonds. We assume that just such interaction of double bonds in the 1,5 position creates the conditions for the development of hydrochlorination by a chain intramolecular mechanism. The greater activity of inner double bonds towards hydrogen chloride compared with vinyl bonds[37,50] is interesting.

The hydrochlorination of polyisoprenes in latex has been studied in detail[47,49,51–53]. At normal pressure the reaction rate in very low, owing to the low rate of diffusion of hydrogen chloride in the latex globules. Raising the pressure to 2 atm increases the reaction rate tenfold. Here the concentration of hydrogen chloride in the latex is increased by only a few per cent. The reaction has a negative temperature coefficient. The hydrochlorination of natural *cis*-polyisoprene in latex reaches 98–99%, and cyclisation is absent.

The addition of hydrogen bromide to natural *cis*-polyisoprene in the presence of peroxide takes place by a radical mechanism with the formation of a secondary bromide[37]. A kinetic analysis of the hydrobromination products showed the high activity of bromine in the addition products characteristic of tertiary bromides. Tuot[54] explains this by the influence of the methyl group situated in the α position to the secondary bromine. With secondary chlorides such an influence of the methyl group on the reactivity of the chlorine is not observed.

3. Hydrogenation

Hydrogenation occupies a special place in the chemistry of diene polymers. In the classical studies of the hydrogenation of natural rubber, made by Staudinger[55] and Pummerer[56], a series of important observations were made and the concept of macromolecules was formulated. Recently the hydrogenation of polyisoprene has been studied by Yakubchik and coworkers[57]. Natural and synthetic *cis*-polyisoprenes at 0.5% concentration in decalin are hydrogenated on a nickel catalyst at 80–140°C and a pressure of 80–100 atm, in the presence of 1% antioxidant. Synthetic polyisoprene, which has a lower molecular weight, is hydrogenated more readily; in the opinion of the authors this is due to the greater mobility of segments of its macromolecules as compared with natural *cis*-polyisoprene. The extent of the reaction increases with the temperature and with increase in the amount of catalyst. The maximal extent of the reaction is ~ 80% saturation of the double bonds. Spectrochemical analysis showed the absence of *trans*-links in the hydrogenation product. The refractive index

decreases linearly with the extent of reaction, on the basis of which the authors conclude that there is no cyclisation. However, this conclusion requires additional proof, since a decrease in refractive index due to decrease in the number of double bonds can exceed its increase due to cyclisation.

Bateman and coworkers[58] noted a diminished reactivity for natural *cis*-polyisoprene compared with the low-molecular model alkenes in the hydrogenation. Evidently this is connected with the reduction in electron density of the double bonds in 1,5-polyene systems due to the interaction of the double bonds. As already noted above, the interaction of double bonds in such systems creates conditions for the development of reactions of 1,5-polyenes by an intramolecular chain mechanism.

The hydrogenation of polybutadiene has received great attention. Jones[59] studied its hydrogenation on a nickel catalyst at 140–180°C; the quantity of catalyst employed is the determining factor in the reaction. The introduction of all the catalyst at once is more effective than its introduction in portions. The temperature has a marked effect on the extent of the reaction. Raising the temperature from 140° to 180°C reduces the unsaturation of the product from 34.6% to 9.5%.

Degradation of the polymer does not take place in the hydrogenation. According to infrared spectroscopy, the vinyl bonds are hydrogenated somewhat more rapidly than the inner double bonds, but at a residual unsaturation of 20%, vinyl groups are still present.

Yakubchik and coworkers[60,61] studied the hydrogenation of a polybutadiene with 57% 1,4-structure in heptane and hexane at 20°C on a nickel catalyst at a pressure of 1 atm. Varying the concentration of the solution within the range 0.2–0.8% did not affect the reaction. The reaction was finished in 20–30 min when its extent was ~ 60%. Apparently cyclisation was absent, as was shown by the diminished refractive index. The relative viscosity was somewhat reduced, owing to a change in the configuration of the macromolecules, but the molecular weight remained constant. For hydrogenation in iso-octane at 60–140°C the reaction rate was almost independent of temperature.

The hydrogenation of *cis*-polybutadiene (unsaturation 95% of theoretical, 5% *trans*-1,4-units, 6% vinyl bonds) was investigated in decalin in the presence of 1% Neozon D, on palladium, platinum, and nickel catalysts[62–64]. Whereas the hydrogenation of low-molecular alkenes proceeds at constant rate up to 50% conversion, the rate of hydrogenation of the macromolecules of *cis*-polybutadiene drops during the course of the reaction owing to the marked change in the rigidity of the chain, accompanied by a sharp rise in viscosity on going from a polydiene with a *cis*-configuration to a saturated polyethylene. Non-regular polybutadiene does not exhibit the flexibility of *cis*-polybutadiene, therefore its hydrogenation is not accompanied by so significant an increase in viscosity.

In the hydrogenation of an unfractionated specimen of polybutadiene a mixture of macromolecules with different degrees of unsaturation is formed[65–67]. This non-homogeneity of the hydrogenation products may be due both to the heterogenic nature of the reaction, the influence of the molecular weight of the polymer, and also to the interaction of the double bonds in the 1,5-polyene systems.

Fractionation of the products of the incomplete hydrogenation of sodium butadiene rubber on a palladium catalyst leads to the production of a fraction with a marked difference in unsaturation (see Table)[66,67].

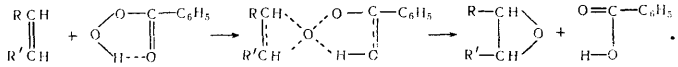
Polybutadiene can also be hydrogenated under homogeneous conditions in the presence of a soluble catalytic system of the Ziegler type[68,69]. The tri-isobutylaluminium–isopropyl titanate system can be used as the catalyst. The hydrogenation is effected in an autoclave at a pressure of 2–5 atm, 20–70°C, for 2–4 h. The ratio of the metal in the organometallic component to the transition metal is varied from 3 : 1 to 10 : 1.

As compared with the heterogeneous reaction, homogeneous hydrogenation permits a marked decrease in the amount of catalyst in the system, a reduction in the temperature and pressure, and there is less destruction of the polymer. Nothing has been published about the fractionation of the products of incomplete hydrogenation under homogeneous conditions.

4. Reaction with Perbenzoic Acid

The reaction of unsaturated compounds with perbenzoic acid was studied in detail by Prilezhaev[70–72]. It was found that the rate of reaction depends on the position and nature of the substituent at the double bond. The main reaction path yields epoxy-groups in an amount equivalent to the benzoic acid formed.

Apparently this reaction proceeds by a molecular mechanism as a result of the direct addition of oxygen at the site of the double bond[73]:



Chloroform and chlorobenzene are usually employed as solvents for carrying out reactions with diene polymers[73–80]. The reaction rate is increased fivefold on going from 6° to 24°C, but with rise in temperature side-reactions begin to occur.

Electronegative oxygen-containing groups (ether, carboxyl, aldehyde) at a double bond retard the reaction, alkyl groups accelerate the addition of perbenzoic acid. The difference in the rates of reaction of *cis*- and *trans*-double bonds is comparatively small. The rate of reaction of terminal and vinyl double bonds is less than the rate of reaction of the internal double bonds. The last fact forms the basis of a kinetic method of determining the structure of diene polymers developed by Dogadkin and Dobromyslova[75].

TABLE. Fractionation of the products of the hydrogenation of sodium butadiene rubber in the pentane–dioxan system

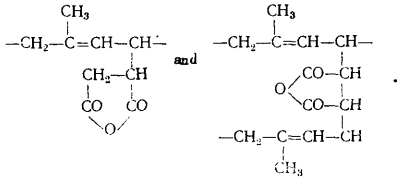
Specimen fractionated	Fraction No.	Weight fraction, %	Unsaturation, %
Hydropolybutadiene with 42% unsaturation	1	22.3	1.0
	2	18.6	1.5
	3	3.0	2.6
	4	29.4	66.0
	5	26.8	77.2
Hydropolybutadiene with 24% unsaturation	1	50.0	1.0
	2	7.0	1.6
	3	10.6	1.0
	4	5.4	4.0
	5	27.0	66.0

III. REACTIONS INVOLVING THE PARTICIPATION OF DOUBLE AND ALLYL BONDS

1. Reaction with Ethylenic Monomers

The reaction of maleic anhydride with natural polyisoprene was first examined by Bacon and Farmer[81]. The reaction was carried out in the presence of benzoyl peroxide at 100°C. The extent of the reaction is proportional to the concentration of the peroxide and the remaining concentration of maleic anhydride. The best solvents for carrying out the reaction are carbon tetrachloride, decalin, and cyclohexane. In benzene, toluene, and xylene reaction is slight. At polymer concentrations $> 3\%$ or at a peroxide concentration $> 1\%$, calculated on the rubber, gel formation takes place. Temperature has little effect on the reaction. The authors assume that each molecule of the anhydride is attached to two double bonds of the polyisoprene, neighbours in a single macromolecule, adjacent in two macromolecules, or adjacent in a single macromolecule.

Later, Farmer proposed a different reaction mechanism with participation of α-methylene groups[86]. The double bonds do not participate in the reaction. The addition products are represented by the formulae:



Delalande[82-84] investigated the reaction of polyisoprenes with ethylene monomers under the conditions of thorough purification of the polymer and complete exclusion of oxygen from the reaction medium. *N*-methylmaleimide was used instead of maleic anhydride, which allowed the extent of the reaction to be determined from the proportion of bound nitrogen in the polymer. *p*-Bromobenzoyl peroxide was used instead of benzoyl peroxide, and its addition was determined from the amount of bromine in the reaction products. The reaction was carried out at 60–130°C. At higher reaction temperatures less gel was formed. At a peroxide concentrations $> 3\%$, gel formation was observed at any temperatures.

With increase in the concentration of the imide and peroxide the extent of the reaction increases. It was found that half the peroxide radicals add to the polyisoprene, the other half form an acid.

The reaction takes place in two stages. In the first stage of the reaction at 130°C there is a rapid addition of the imide and peroxide, then follows the second stage—the addition of the imide without the peroxide. The rate of the second stage is less by a factor of 200. Reducing the temperature from 130° to 60°C cuts the reaction rate by a factor of 130.

In addition to the kinetics of addition, the change in the degree of unsaturation of the polyisoprene in the reaction was studied by an iodometric method. The decrease in the unsaturated nature is always less than theoretical (assuming the imide was added to the double bond) and correlates better with the addition of peroxide radicals. The reaction proceeds according to the following scheme. Initially the peroxide decomposes into radicals:

$$AA \rightleftarrows 2A^{*} .$$

Then a peroxide radical detaches an α-methylene hydrogen of the polyisoprene

$$A^{*} + RH \rightarrow AH + R^{*} .$$

The macroradical formed reacts with the double bond of the imide:

$$R^{*} + E \rightarrow RE^{*} .$$

The macroradical which is formed detaches an α-methylene hydrogen from another polyisoprene molecule, etc.:

$$RE^{*} + RH \rightarrow REH + R^{*} .$$

Kinetic studies at 170°C in the absence of peroxide were carried out with the aim of explaining the mechanism of the slow stage of the reaction[84]. Gel formation is not observed at a concentration of polyisoprene in the solution up to 10%. At 170°C the amount of imide attached is seven times that at 110°C. The rate and extent of the thermal reaction increase with the initial concentrations of imide and polyisoprene.

The change in the unsaturation of the polymer during the thermal reaction was determined iodometrically and bromometrically. The values obtained by the second method were lower by a factor of two. In both instances the decrease in unsaturation is significantly less than theoretical (addition of imide at the double bond), which shows that the reaction proceeds by substitution. The considerably greater yield of double bonds in the iodometric determination is evidently connected with the fact that the bromine atom adds more readily at the double bond whereas the larger iodine atom is hindered by the imide moiety attached directly to the double bond. The small real change in unsaturation is probably due to cyclisation of the polyisoprene.

Delalande proposes the following mechanism for the thermal reaction of *N*-methylmaleimide with polyisoprene. Initially the double bond of the imide is opened, with the formation of a biradical:

$$E \rightarrow E^{**} .$$

The biradical detaches an α-methylene hydrogen from a polyisoprene molecule:

$$E^{**} + RH \rightarrow {}^{*}EH + R^{*} .$$

The macroradical which is formed adds the imide at the double bond:

$$R^{*} + E \rightarrow RE^{*} .$$

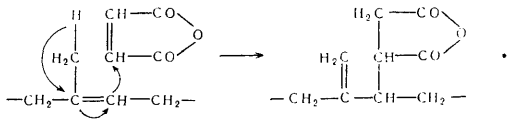
The re-formed macroradical reacts with the following polyisoprene molecule:

$$RE^{*} + RH \rightarrow REH + R^{*} .$$

Pinazzi and coworkers[85] and de Merlier and Le Bras[86] cast doubt on the radical nature of the thermal reaction, since thiophenol, which is a strong acceptor of radicals, has no effect on the thermal reaction although it retards the radical reaction which takes place in the presence of peroxide.

The presence of maleic anhydride was observed spectroscopically in the products of its reaction with polyisoprene in the presence of initiators[85]. Saturation of the double

bonds of polyisoprene or their isomerisation is not observed. In the thermal reaction (without initiator) the unsaturation of the polyisoprene does not alter and the reaction proceeds according to the scheme:



The NMR studies confirm the displacement of the double bond.

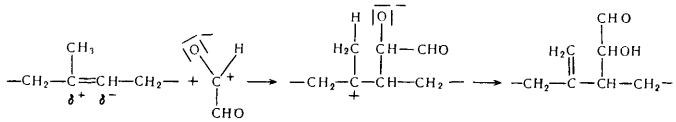
The more readily an ethylene monomer is polymerised, the greater the amount of graft polymer formed in its reaction with diene polymers. The ethylenic monomers with diminished electronic density of the double bond are readily added to *cis*-polyisoprene (maleic anhydride, γ-crotonolactone, *N*-methylmaleimide, fumaric and maleic acids, *p*-benzoquinone, acrylonitrile, chloromaleic anhydride) when there is no steric hindrance (fumarodinitrile, vinylidene chloride, etc.).

Monomers with enhanced electron density at the double bond (styrene, allyl alcohol) or with normal electron density (cyclohexene, indene) do not react with *cis*-polyisoprene.

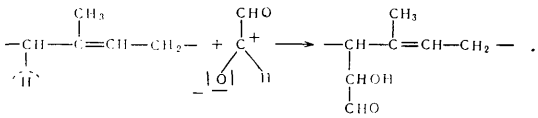
2. Reaction with Aldehydes

Pinazzi and Pautrat[87,88,91] investigated the reaction of *cis*-polyisoprene with glyoxal in xylene, under conditions where oxygen was thoroughly excluded from the reaction medium. The reaction was carried out at 25–180°C and the extent of the reaction was estimated from the oxygen content of the product. The reaction of glyoxal with polyisoprene is accompanied by a considerable gel formation, especially at low temperatures. At 180°C a soluble product can be obtained if the amount of glyoxal does not exceed 40 mole %, calculated on the polymer.

Usually, 24–32 moles glyoxal are added per 100 isoprene units. Examination of the reaction products by infrared spectroscopy and chemical analysis showed the presence of carbonyl and hydroxyl groups. The authors propose the following reaction mechanism:



and also assume that reaction can occur by the scheme:



The products of the reaction of glyoxal with polyisoprene are not homogeneous: unreacted polyisoprene could be extracted from the reaction medium; the amount extracted increased with decrease in temperature.

The reaction of natural *cis*-polyisoprene with chloral[89–91] has been investigated in solution in cyclohexane and decalin, free from peroxides. The reaction was carried out in an inert atmosphere (pure nitrogen) in the presence of 1–3% catalyst ($AlCl_3$, BF_3), calculated on the polyisoprene, at a polymer concentration in the solution of 2%. The product was fractionated in a methanol–chloroform mixture. For the main fraction, the concentration of combined chlorine gave the number of added molecules of chloral per 100 polyisoprene units (n). The reaction temperature was varied between 25° and 200°C and the excess of chloral from 0 to 1000%.

In the absence of a catalyst the reaction did not proceed far ($n = 3$) and was almost independent of temperature. In the range 25–180°C boron trifluoride is the more efficient catalyst; in the range 180–200°C, aluminium chloride is better. The catalyst efficiency increases with the temperature.

Increasing the excess of chloral to 300% leads to an increased extent of reaction, but a further increase has hardly any effect on it. The reaction of chloral with polyisoprene is accompanied by gel formation, the intensity of which depends on the type of catalyst (greatest gel formation on using $HgCl_2$, least with $AlCl_3$).

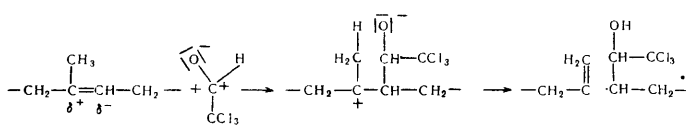
The effect of radical acceptors on the extent of reaction was investigated. The introduction of 3% thiophenol, *p*-benzoquinone, nitrobenzene, or sodium diethyldithiocarbamate had hardly any effect on the reaction of chloral with polyisoprene. To show whether a radical mechanism was possible, the reaction of chloral with polyisoprene in the absence of catalysts was studied. The initiators used were peroxides, azo-compounds, disulphides, and ultraviolet irradiation; all were ineffective.

The maximal addition ($n = 22$) was obtained by carrying out the reaction in cyclohexane at 180°C with aluminium chloride (3%) and a 300% excess of chloral. In the absence of a solvent at 180°C the reaction proceeds to $n = 5.5$. With thorough purification of the *cis*-polyisoprene the same results are obtained as for natural *cis*-polyisoprene. On carrying out the reaction with butyl rubber (3.5% isoprene) more than half of the double bonds react with the chloral. The extent of the reaction of *cis*-polybutadiene with chloral is very slight ($n = 1.5$).

Infrared analysis of the products of the addition of chloral to *cis*-polyisoprene showed the presence of hydroxyl groups (3300–3500 cm^{-1}) and chlorine (570, 620, 680, 730, and 1080 cm^{-1}), that is, the side chain has the structure $-CHOH-CCl_3$.

The characteristic frequencies of the cis-1,4-structure are weakened. The broadening of the 1640 cm^{-1} peak and the appearance of a band at 860 cm^{-1} show the formation of vinyldiene double bonds. The presence of a $-CHOH-CCl_3$ group has also been shown by chemical methods (reaction with sodium, phenyl-lithium, acetyl chloride, and alcoholic solution of potassium hydroxide). The appearance of absorption bands at 770 and 1040 cm^{-1} and also the decrease in the viscosity of the polymer during the reaction shows that cyclisation takes place. There is little cyclisation in the presence of aluminium chloride and extremely little when boron trifluoride is used.

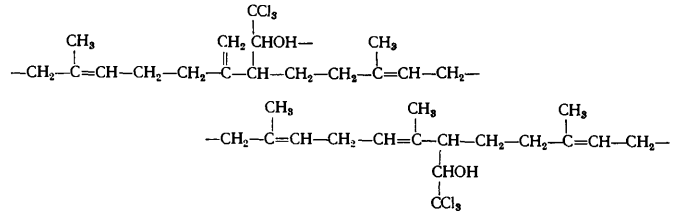
The addition of chloral proceeds at random along the chain. The probable reaction mechanism is:



The reaction mechanism for *cis*-polybutadiene is different. Here the group added is $-CCl_2-CHO$, as is shown by the appearance in the spectrum of a band at 1780 cm^{-1},

characteristic for the carbonyl group, and the absence of the absorption band for hydroxyl.

The different reaction mechanisms for polyisoprene and polybutadiene with glyoxal can be explained as follows. The Prins reaction presumes the migration of a double bond with change of a methyl group into an exomethylene group or migration along the chain for polyisoprene.



and only along the chain for polybutadiene. The migration of one double bond along the chain reduces the effectiveness of the utilisation of the electrons in at least three isoprene units, since two double bonds prove to be in the 1,4-position, and two in the 1,6-position [13]. Hence the increase in the free energy of the system with the breakdown of the 1,5-sequence in the double bond alternation prevents the reaction with migration of a double bond.

3. Reaction with Molecular Chlorine

One of the most widely studied reactions of diene polymers is the chlorination of polyisoprenes and polybutadienes. Bloomfield's classical investigations allowed three main stages in the chlorination of natural rubber to be distinguished. In the first stage a molecule of chlorine reacts with an isoprene unit wholly by substitution:

$$C_{10}H_{16} + 2\,Cl_2 \rightarrow C_{10}H_{14}Cl_2\ (34.6\%\ Cl) + 2\,HCl\ .$$

In the second stage addition and substitution occur:

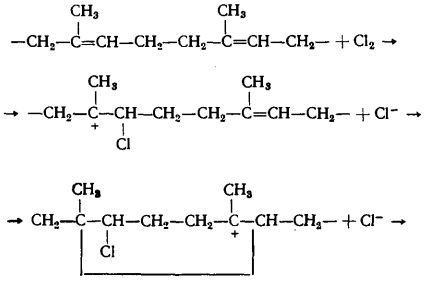
$$C_{10}H_{14}Cl_2 + 2\,Cl_2 \rightarrow C_{10}H_{13}Cl_5\ (57.2\%\ Cl) + HCl\ .$$

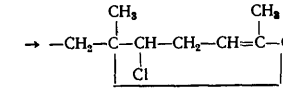
In the third stage there is only substitution:

$$C_{10}H_{13}Cl_5 + 2\,Cl_2 \rightarrow C_{10}H_{11}Cl_7\ (65.4\%\ Cl) + 2\,HCl\ .$$

The reaction was carried out in carbon tetrachloride in the temperature range −80° to +77°C, in the dark and in the light. The concentration of chlorine in the reaction products was determined by product analysis.

The chlorination of natural polyisoprene is accompanied a considerable drop in the viscosity of the solution (factor of 2–7) owing to the simultaneous occurrence of cyclisation (Bloomfield ascribes this effect to oxidation). At low temperatures cyclisation is insignificant and viscosity is reduced by a factor of 1.3. In the first stage of the reaction the unsaturation in the polymer diminishes (iodometric determination). Bloomfield suggests the following mechanism for cyclisation during chlorination:





Staudinger [40] suggests that cyclisation takes place with participation of the methyl groups.

Apart from cyclisation, the decrease in unsaturation shown iodometrically can be due to steric hindrance of the double bonds by neighbouring chlorine.

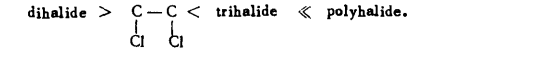
The chlorination of natural rubber does not take place by a radical mechanism since light, oxygen, peroxides, and antioxidants do not affect the reaction. When using sulphuryl chloride and phenyl dichloroiodate a radical mechanism of chlorination leads to the addition of chlorine at the double bond. An attempt was made to form radicals from molecular chlorine by irradiation and the introduction of peroxides. However, here also not addition of but substitution by chlorine was observed.

Kraus and Reynolds [93] investigated the chlorination of natural *cis*- and *trans*-synthetic polyisoprenes. The latter contained 90% *cis*- and *trans*-1,4-structures and 10% of the 1,2-structures. The properties of the chlorinated products were identical. The complete identity of natural *cis*- and *trans*-polyisoprenes on chlorination in the presence of antioxidant has been noted. The chlorination of synthetic polyisoprene proceeds similarly when the reaction takes place in the dark. In the light and in the presence of 0.3% oxygen (antioxidant absent) the addition to synthetic polyisoprene occurs even in the first stage of the reaction, and is increased on ultraviolet irradiation in the presence of 1% benzoyl peroxide.

Cyclisation is less pronounced in synthetic polyisoprene owing to the irregularity of the structure. In the early stages of the chlorination there is formation of one ring per three substitutions of chlorine. Until cyclisation has finished chlorine does not add to double bonds apart from those which are formed as a result of cyclisation and the vinyl bonds. In the presence of light and peroxides this rule is broken and addition proceeds at the expense of cyclisation.

A series of papers by Van Amerongen and coworkers [94-99] is devoted to the detailed explanation of the reaction mechanism of the chlorination of natural rubber. The structure of the products of the halogenation of rubber was determined by kinetic analysis, from the rate of reaction of the chloride with organic bases. Depending on the structure of the monochloride, the various types of chlorine are arranged in the following series of activity relative to aniline: allyl > tertiary ≫ primary > secondary ≫ ≫ vinyl.

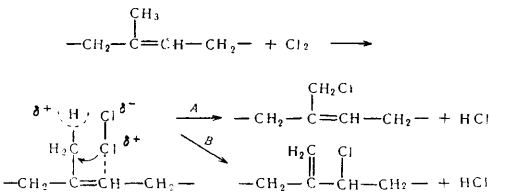
The order of reactivity of polyhalides has the following form:



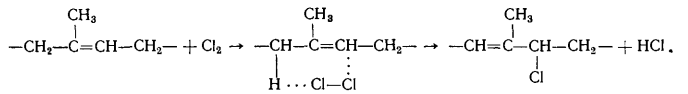
Kinetic investigations showed that the higher the chlorine content of the reaction product the more stable it is. The stability of the chlorination products depends on the total chlorine content and is independent of such experimental conditions as the presence of light or catalysts, temperature, chlorine pressure, or the effecting of the reaction in bulk or in solution with liquid or gaseous chlorine. This shows that the sequence of stages is retained during chlorination under different conditions: at first there is substitution then addition at the double bonds.

When there is less than 25% chlorine in the chloride of natural *cis*-polyisoprene, all the chlorine is allyl, as is shown by its high reactivity in the aniline experiment. In products with 65% chlorine the content of allyl chloride drops to 10%, owing to saturation of the double bonds. Further chlorination leads to an increase in the percentage of reactive chlorine due to the formation of the dichloride $-CCl_2-$.

Bloomfield and Van Amerongen and their coworkers adopt an ionic mechanism for the chlorination of diene polymers. The heterolytic breaking of a purely covalent bond seems improbable to us. The reaction of chlorine with a double bond by a molecular mechanism is more probable, as McNeill believes [100] for the chlorination of butyl rubber:



When an α-methylene group participates in the reaction (for polybutadiene of 1,4-structure this is the only possibility) the double bond migrates along the macromolecular chain:



Whereas for the isolated double bonds of butyl rubber the migration of a double bond along a chain during chlorination does not encounter hindrance, a similar migration of one double bond in a 1,5-polyene chain should be accompanied by an increase in the free energy of the system owing to the breakdown of the condition of delocalisation of three double bonds, as was shown by the example of the reaction of polybutadiene or polyisoprene with chloral. However, when the intermediate complexes form successive links of a polymeric chain and the macromolecule or part of it changes into a collective excited state, forming a cooperative intermediate complex (CIC); the decomposition of such a CIC of any dimensions will be accompanied by the breakdown of interaction of only four double bonds (two at each end of the CIC). At the same time the gain in energy during the breakdown of the CIC to form addition products will increase additively with the inclusion in the CIC of each new link of the macromolecule and can considerably exceed the increase in energy of the system due to the breakdown of the conditions for the interaction of four double bonds. Hence a reaction of cooperative interaction can take place where a single addition with migration of a double bond along the chain is impossible.

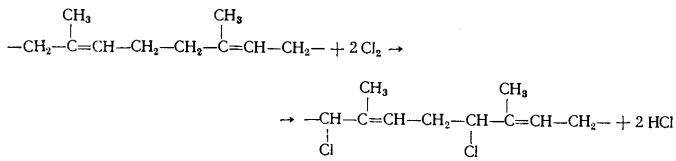
The formation of a CIC in reactions of diene polymers is favoured by the fact that the production of one intermediate complex facilitates the formation of analogous complexes by neighbouring links of a macromolecule owing to the increased reactivity of the double bonds in the 1,5-position relative to those which have reacted.

The cooperative mechanism for the first stage of the chlorination of polyisoprene provides an explanation for the fact that at this stage double bonds do not participate in cyclisation and addition [92,101]. If it be assumed that a CIC embraces the whole macromolecule it becomes understandable that double bonds can no longer participate in reactions up to the decomposition of the CIC with regeneration of double bonds in a new position.

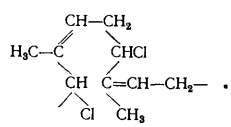
The products of incomplete chlorination of natural *cis*-polyisoprene (up to 30% bound chlorine) are non-homogeneous [94,101] even when chlorine dissolved in carbon tetrachloride is added dropwise to a solution of polyisoprene with vigorous stirring. In the chlorination products there is always a fraction with 31–33% chlorine [101]. With 34–35% chlorine the product is almost homogeneous, and the same is true for products with a higher content of chlorine [102]. According to Bloomfield 35% chlorine in the product corresponds to the end of the first stage of reaction, When the total chlorine in the product is $< 30\%$, 90–95% of this chlorine is reactive. Van Amerongen [94] explains the non-homogeneity of the product of incomplete chlorination by a high reaction rate in the first stage and by the existence of a zone of high concentration owing to the high viscosity of the solution. Trousier [101] considers that for a chlorine concentration of $< 34\%$ the chlorine which has been added favours the extension of the macromolecule, which facilitates further addition of chlorine to the same macromolecule. The viscosity results do not confirm this point of view. We assume that the reason for the products of the first stage of chlorination of polyisoprene being non-homogeneous is the cooperative intramolecular chain mechanism of the reaction.

An infrared analysis of the products of the chlorination of natural *cis*-polyisoprene [97,101,103–105] showed a weakening of the 3.4 μm (C–H bond) and 12 μm (*cis*-C=C) absorption bands until the latter disappeared completely during the chlorination. The 6 μm band ascribed to the C=C bond is constant up to 35% chlorine, then rises, but disappears at the end of chlorination. The intensity of the 6.9 μm band (C–H bond) remains constant. The 8 μm band (ring) appears at 35% chlorine and then rises. The 11 μm band (ring) appears during chlorination but its intensity falls for chlorine concentrations $> 35\%$.

Salomon and coworkers [97] ascribe the change in intensity of the 6 μm band and the appearance of the 11 μm band to the formation of vinyl bonds during chlorination. Allirot and Orsini [105] note a marked similarity between the spectra of the chlorides of polyisoprene and cyclohexane, and consider this to be confirmation of the cyclic structure of chlorinated polyisoprene. Trousier [101] considers that the changes in the spectrum are great only in the first stage of chlorination and ascribe them all to cyclisation. He represents the cyclisation mechanism as follows. After the first stage of chlorination:

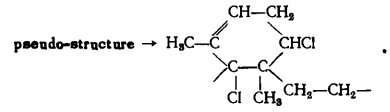


a pseudocyclic structure is formed:



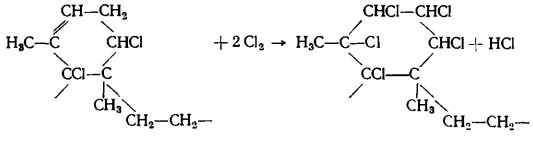
During this there are no significant changes in the spectrum, but a decrease in viscosity shows the contraction of

the macromolecular chains. Until the molecule is saturated with 35% Cl it does not cyclise. On reaching this threshold the individual macromolecules are cyclised according to the scheme:

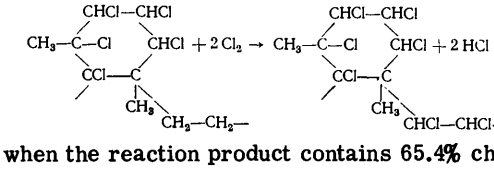


The results of the kinetic analysis confirm this picture: when the chlorine content of the reaction product is < 35% all the chlorine is allyl; on reaching 35% bound chlorine there is a sharp drop in the allyl chlorine content—its amount is cut by half. Further chlorination is accompanied by an increase in the reactive chlorine content; starting from 45% bound chlorine, the fraction of reactive chlorine drops monotonically.

The drop in viscosity stops after completion of the first stage of chlorination. Further chlorination proceeds under the condition that all the product was cyclised and there are no macromolecules with < 35% chlorine.



The products of this stage of chlorination are homogeneous. Substitution predominates over addition, as is shown by the increased content of allyl chlorine. The final stage of chlorination—the substitution



—ends when the reaction product contains 65.4% chlorine.

Ramakrishnan [106] studied the change in the unsaturation of natural *cis*-polyisoprene during chlorination by ozonation of the reaction products. A 4% solution of the polymer in carbon tetrachloride was saturated with gaseous chlorine at 2° and 78°C. With the aim of excluding the addition of hydrogen chloride formed in the substitution reaction, nitrogen was bubbled through the solution. The results obtained agree with the chlorination mechanism proposed by Trousier.

Canterino [107] notes the marked influence of the solvent on the chlorination of natural *cis*-polyisoprene. When the reaction is carried out in benzene hardly any cyclisation is observed—the double bonds do not disappear and the viscosity does not change. In the presence of phosphorus(III) chloride the cyclisation is greatly accelerated.

The chlorination of polybutadiene emulsion [107] proceeds somewhat more slowly and the product is more stable. When the reaction is carried out in carbon tetrachloride a cross-linked product is obtained; in benzene, chloroform, toluene, and tetrachloroethane, gel formation does not take place. The introduction into the reaction of iodine, phosphorus(III) chloride, phosphorus(V) chloride, or sulphuryl chloride prevents cross-linking, the phosphorus chlorides being the most effective in this respect. The chlorination products do not contain phosphorus. The substitution in polybutadiene is less pronounced than that in *cis*-polyisoprene and diminishes on going from carbon tetrachloride to benzene. The cyclisation occurs weakly in benzene, somewhat more in carbon tetrachloride, and is absent in both instances when phosphorus(III) chloride is used.

Van Amerongen [98] described the chlorination of natural and polychloroprene latex in strongly acid medium with an emulsifier. The latex concentration was 30–55% and the reaction was carried out at 15–90°C. Natural latex was chlorinated up to 60% combined chlorine in the reaction product, and the polychloroprene latex up to 48% combined chlorine. Within the limits given the temperature had hardly any effect on the rate or extent of the reaction.

4. Reaction with Bromine and Other Halogenating Agents

The quantitative addition of bromine at double bonds with the formation of a tetrabromide is used in gravimetric analysis [108–111]:

$$(C_{10}H_{16})_n + 2n Br_2 \rightarrow (C_{10}H_{15}Br_4)_n$$

and in volumetric [112–114] methods of determining the unsaturation of diene polymers. The rate of bromination of the polyisoprenes increases with the temperature, but at temperatures above 0°C the addition of bromine is accompanied by substitutions and cyclisations [115–119]. The usual solvents employed for the reaction are benzene, chloroform, and carbon tetrachloride. Radiation accelerates the reaction but favours substitution. Substitution can be suppressed by use of a polar reagent (glacial acetic acid) [116].

The bromination of *cis*-polybutadiene was investigated at temperatures between 0° and −20°C in chloroform. Under these conditions there is only addition of bromine at the double bonds; cleavage, substitution, and cyclisation do not take place [120].

The products of the incomplete bromination of natural rubber and gutta-percha are not homogeneous [13, 121]. The bromination [13] was carried out in benzene (0.3% solution of polyisoprene), and the brominating solution (5% bromine in carbon tetrachloride) was introduced with cooling with ice and vigorous stirring. The amount of bromine corresponded to the theoretical for the desired degree of bromination.

To obtain homogeneous products from an incomplete bromination, various procedures were tried, mainly based on the introduction of a third component, but none of them gave positive results. Evidently the bromination does not obey statistical laws and takes place by the intramolecular chain mechanism considered above.

On reacting with polyisoprenes [96], sulphuryl chloride forms a dichloride when the polymer has been thoroughly purified; otherwise, substitution is observed. At high temperatures or in the presence of iodine, the sulphuryl chloride decomposes and the chlorination of the rubber under these conditions follows the usual path. At 40–60°C in the light and in the presence of a catalyst (pyridine), sulphuryl chloride is added at the double bonds. In the presence of initiators (ascaridole, benzoyl peroxide), the Kharasch reaction takes place:

$$\text{peroxide} \rightleftarrows 2R^*$$

$$R^* + SO_2Cl_2 \rightarrow RCl + SO_2Cl^*$$

$$SO_2Cl^* \rightarrow SO_2 + Cl^*$$

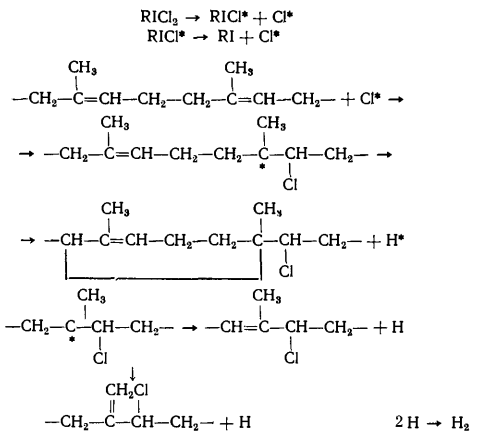
$$Cl^* + >C{=}C< \rightarrow >C(Cl)-C^*<$$

$$>C(Cl)-C^*< + SO_2Cl_2 \rightarrow >C(Cl)-C(Cl)< + SO_2Cl^* \cdot$$

The reaction of sulphuryl chloride with natural *trans*-polyisoprene was investigated at 5–77°C in carbon tetrachloride. The presence of peroxide and ultraviolet radiation accelerates reaction. The content of reactive chlorine, capable of reaction with aniline, was always 5–7%. Little hydrogen chloride was formed. The temperature had little effect on the reaction. In the presence of inhibitors (hydroquinone, 2-naphthol) the reaction is slow and proceeds by substitution (~ 70% reactive chlorine), to a slight extent. Amino- and nitroso-compounds have a similar effect on the reaction.

The reaction of sulphuryl chloride with polyisoprenes is accompanied by gel formation, the extent of which increases with drop in temperature (when the rate of gel formation decreases), on irradiation, and in the presence of traces of water. Antioxidants do not affect the gel formation but nitrogen oxides hinder it. The introduction of 5% hydroperoxides, hydrogen iodide, iodine, or chlorine leads to a drop in the viscosity of the solution. Apparently hydrogen iodide deactivates radicals, leading to the cross-linking of the macromolecules; chlorine and peroxides break down the cross-linking.

In accordance with Bloomfield's results [122] phenyl dichloroiodate forms the dichloride almost exclusively when it reacts with natural *cis*-polyisoprene in the absence of oxygen. There is considerable substitution in the presence of inhibitors. Ramakrishnan [123], who studied the reaction products by use of ozonisation, considers that as well as the addition of chlorine at the double bonds, cyclisation, depolymerisation, decyclisation, and migration of double bonds with the release of a proton take place. The reaction mechanism is described by the following scheme:

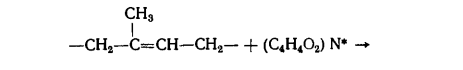


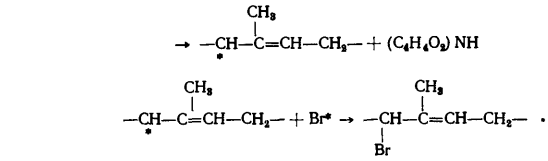
The migration of the double bond with release of a free proton is improbable. It was found that the release of hydrogen chloride in the individual stages of the reaction does not exceed 1–2%, and atmospheric oxygen has no effect on the reaction.

Bromination with *N*-bromosuccinimide [120] takes place through a change in the radical nature of the reaction. The first stage of the reaction is the decomposition of *N*-bromosuccinimide into radicals:

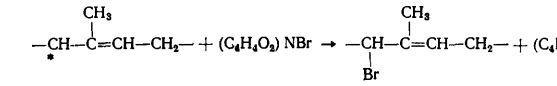
$$(C_4H_4O_2)NBr \rightarrow (C_4H_3O_2)N^{\bullet} + Br^{\bullet}.$$

The radicals formed react with the polyisoprene:





The macroradical can also react with the following molecule of *N*-bromosuccinimide:

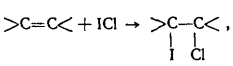


Cyclisation takes place simultaneously.

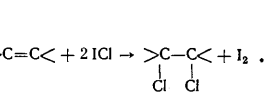
Iodine chloride adds quantitatively to polybutadiene when the reaction is carried out in a non-polar solvent at 25°C with an excess of iodine chloride [116]. In dichloroethane the addition is accompanied by substitution. For polyisoprene of non-regular structure the addition of iodine chloride is accompanied by substitution and cleavage. The hydrogen iodide liberated in the last two reactions reacts with iodine chloride to form molecular iodine:

$$HI + ICl \rightarrow HCl + I_2.$$

The addition of chlorine iodide proceeds according to the scheme:



and not as follows



The reaction takes place by an ionic mechanism and initiators and inhibitors of radical reactions have no effect on it. The presence of alkyl groups at the double bond accelerate the addition, a halogen atom at the double bond retards the reaction. It is suggested that an internal double bond should react 2–4 times more rapidly than a vinyl group [119]. According to their activity in relation to iodine chloride, diene polymers form the following series: polyisoprene > polybutadiene > polychloroprene. When there are conjugated bonds the iodine chloride rapidly adds to the first bond and slowly to the second.

Iodine bromide adds to polybutadiene in carbon tetrachloride without release of hydrogen halide [124]. The formation of hydrogen iodide increases with the solvent used in the following order: chloroform–dichloroethane–tetrachloroethane. Ultraviolet irradiation assists substitution. The liberation of hydrogen iodide is much greater with polyisoprene.

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The above analysis of the reactions of diene polymers allows us to find characteristics for 1,5-polyene systems, consisting in the interaction of the double bonds, the reduction of their reactivity, and the possibility of development of the reactions of such systems according to an intramolecular chain mechanism. Such interaction of double bonds greatly complicates the solution of practical problems connected with the treatment and stabilisation of diene polymers. Thus for vulcanisation the development of reactions by an intramolecular chain mechanism should lead to

an extremely inefficient use of the vulcanising agent and to an undesirable modification of the polymeric chains which actually occurs during sulphur vulcanisation, especially in the absence of an accelerator. The autocatalytic nature of the oxidation of 1,5-polyenes and the accumulation of oxidation products in separate macromolecules[125] are also evidently connected with the interaction of the double bonds in these polymers. We suggest that detailed study of the possibility of developing the reactions of diene polymers by an intramolecular chain mechanism is now one of the most pressing problems of the chemistry of 1,5-polyenes.

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THE REARRANGEMENT OF HYDRAZO-COMPOUNDS

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1. INTRODUCTION

In spite of the many investigations since the times of Zinin [1] and Hofmann [2], no satisfactory solution has yet been found to the problem of rearrangement as a whole.

The early papers report valuable experimental work. The labours of several chemists (Hofmann [2], Schultz and his coworkers [3-6], Jacobson and his coworkers [7,8], Täuber [9], Witt [10]) during the nineteenth century revealed four types of rearrangement—(1) benzidine, (2) biphenyline, (3) *o*-semidine, (4) *p*-semidine—a fifth rearrangement—*oo'*-biphenyl (in the benzene series)—being discovered by us [11] much later.

Special mention must be made of the work of Jacobson and his collaborators [12] and of Wieland [13], on the basis of which the intramolecular character of the rearrangement was demonstrated. Wieland [14] pointed out the possibility of obtaining hydrazobenzene hydrochloride by the action of dry hydrogen chloride on hydrazobenzene in ether. However, he found that, when certain *para*-substituted hydrazobenzenes were heated in an inert medium, the corresponding semidines were formed [15]. For a long time these observations were not developed further.

During the past two decades attention has been directed mainly at solving by kinetic methods the problem involved in the initial stage of rearrangement in the presence of ionised acids: does the hydrazo-compound react as a univalent or as a bivalent cation? No satisfactory answer has been obtained to this question.

References to what is often termed the "benzidine rearrangement" are usually concerned with the process occurring in an ionised acid medium, as a result of which benzidines and biphenylines [biphenyl-2,4'-diamines] are obtained. Small amounts of other substances are often disregarded.

An important aspect is the very little studied rearrangement in unionised acids. The reaction takes place in a heterogeneous medium, the composition of the products varying greatly with the conditions. The usual methods of investigation employed by organic chemists are applicable to these cases. It is sometimes possible to obtain good yields of monoprotonated hydrazo-compounds and to study some of their properties and reactions. At the same time the stepwise character of the process as a whole is determined: the salt of the hydrazo-compound formed in the first stage rearranges under the further action of the acid.

Not long ago we were able [16] to demonstrate, with hydrazonaphthalenes as examples, a special type of rearrangement produced by the action of heat. This so-called thermal rearrangement is especially complicated in the naphthalene series, where the results are often strongly solvent-dependent.

The present review first describes work on salts of hydrazo-compounds, together with some of their properties and reactions, then discusses rearrangement in acid media, and in conclusion considers rearrangement under the influence of heat.

2. SALTS OF HYDRAZO-COMPOUNDS—SOME OF THEIR PROPERTIES AND REACTIONS

Until recently information on the salts of hydrazo-compounds was confined in effect to Wieland's exploratory experiment [14]. A paper by Orelkin et al., [17] which contained an interesting underlying idea, did not contribute to progress in this field because the experiment was not properly thought out.

Solutions of hydrogen chloride in ether have proved most suitable for the preparation of salts of hydrazo-compounds, and they can be regarded as equilibrium systems:

$$[(C_2H_5)_2\overset{+}{O}H]\,\overline{X} \rightleftarrows (C_2H_5)_2O \ldots HX.$$

Since the acidity of the hydrogen chloride is approximately weakened as a result of intermolecular interaction in the ether, it is easy to prepare hydrochlorides of several hydrazo-compounds. To a solution of the hydrazo-compound, e.g. hydrazobenzene in ether at −8° to −10°C, an equimolecular amount of hydrogen chloride in ether is added rapidly in drops. The hydrochloride is filtered quickly (preferably in an atmosphere of nitrogen), the solution is made alkaline with methanolic sodium hydroxide, and it is oxidised with mercuric oxide, an equivalent quantity of azobenzene being obtained. Salt formation does not go to completion owing to dissociation of the hydrochloride, which is especially marked with the less basic compounds: with 2-chloro- and 3,3′-dichloro-hydrazobenzene, for example, 30–40% of the hydrazo-compound remains [unchanged] in solution, even if double the quantity of hydrogen chloride is taken.

Ethers other than diethyl ether—e.g. di-isopropyl and di-isopentyl ethers—can be used in the preparation of the salts. With hydrogen bromide 40–50% of the hydrobromides of 3-chloro- and 3,3′-dichloro-hydrazobenzene can be isolated.

By no means all hydrazo-compounds form stable salts: it has proved impossible to isolate salts of 4,4′-substituted derivatives. Table 1 gives the yields of salts of several hydrazo-compounds prepared by the method outlined for hydrazobenzene hydrochloride. If in expts. 10 and 20, immediately after precipitation of the hydrochlorides, the whole mixture is made alkaline and is oxidised with mercuric oxide, 70% and 90% respectively of the original hydrazo-compounds are regenerated as the azo-compounds.

Salts of hydrazonaphthalenes cannot be isolated. However, their existence can be demonstrated as follows: 0.002 mole of 1,1′-, 1,2′-, or 2,2′-hydrazonaphthalene is dissolved in the minimum quantity of dioxan, the solution is diluted with ether at −8° to −10°C, and 1 mole of hydrogen chloride in ether is instantly added. A copious, very finely divided precipitate comes down; the whole mixture is made alkaline and oxidised with mercuric oxide as quickly as possible. The initial hydrazo-compounds are regenerated to the extent of 70–75%. Visual inspection shows that precipitates of the hydrochlorides of the corresponding diamines (calculated quantities) are present here in only small amount.

TABLE 1. Salts of hydrazo-compounds, their basic strengths, and rates of rearrangement in 95% acetic acid at 20°C.

Expt. No.	Hydrazo-compound	Yield of hydrazo-salt, %	Chloroaniline with which basic strength is compared	Duration of reaction between hydrazo-cpd. and acetic acid	Loss of hydrazo-cpd., %
1	Hydrazobenzene	92	between 2,4- and 2,5-di-	3 h	50.5
2	2-Chlorohydrazobenzene	66	between 2,4,5-tri- and 2,6-di-	26 h	43.3
3	3-Chlorohydrazobenzene	88	between 2,4,5-tri- and 2,6-di-	146 h	53.1
4	4-Chlorohydrazobenzene	13	between 2,4,5-tri- and 2,6-di-	26 h	64.0
5	2,2′-Dichlorohydrazobenzene	–	≪ 2,3,4,5,6-pentachloro-	720 h	trace
6	3,3′-Dichlorohydrazobenzene	54	between 2,4,6-tri- and 2,3,4,6-tetra-	720 h	3.0
7	4,4′-Dichlorohydrazobenzene	–	< 2,6-dichloro-	120 h	63.0
8	2-Methylhydrazobenzene	13	between 2,5-di- and 2,4,5-tri-	60 min	51.0
9	3-Methylhydrazobenzene	90	< 2,5-dichloro-	60 min	54.0
10	4-Methylhydrazobenzene	22(70)	> 2,5-dichloro-	8 min	57.4
11	2,2′-Dimethylhydrazobenzene	10	2,4,5-trichloro-	8 min	42.5
12	3,3′-Dimethylhydrazobenzene	90	< 2,5-dichloro-	8 min	47.4
13	4,4′-Dimethylhydrazobenzene	–	< 2,4-dichloro-	10 min	33.0*
14	2-Methoxyhydrazobenzene	–	< 2,5-dichloro-	30 s	50.0
15	3-Methoxyhydrazobenzene	26	< 2,5-dichloro-	60 min	50.0
16	4-Methoxyhydrazobenzene	–	–	30 s	40.1*
17	2,2′-Dimethoxyhydrazobenzene	10	between 2,4,5-tri- and 2,6-di-	30 s	53.6*
18	3,3′-Dimethoxyhydrazobenzene	51	> 2,4,5-trichloro-	8 min	32.0
19	4,4′-Dimethoxyhydrazobenzene	–	–	2 s	100.0*
20	2,2′-Diethoxyhydrazobenzene	65(90)	between 2,4,5-tri- and 2,6-di-	10 s	40.0*
21	3,3′-Diethoxyhydrazobenzene	29	> 2,4,5-trichloro-	10 min	40.0
22	4,4′-Diethoxyhydrazobenzene	–	–	2 s	100.0*
23	1,1′-Hydrazonaphthalene	–	–	10 s	40.8*
24	1,2′-Hydrazonaphthalene	–	–	30 s	35.1*
25	2,2′-Hydrazonaphthalene	–	–	60 s	41.8*

* Hydrazo-compound previously dissolved in dioxan.

Basic Strength of Certain Hydrazo-Compounds

Several hydrazo-compounds can be compared in basic strength with chloroanilines. Relatively definite results are obtained with hydrazo-compounds which form the more stable salts.

The procedure is to prepare the hydrobromide of a suitable chloroaniline (0.002 mole) in ether (20 ml), into which is immediately run a solution of the hydrazo-compound (0.002 mole) in ether (20 ml), the temperature lying between −8° to −10°C. After 2 min the precipitate is quickly filtered off (preferably under nitrogen), and both precipitate and solution are made alkaline and are oxidised. The quantity of azo-compound obtained indicates the distribution of the acid between the hydrazo-compound and the chloroaniline†.

With unstable salts of hydrazo-compounds the situation is greatly complicated: a pair of chloroanilines is selected of most closely similar basic strengths, and such that the rearrangement would be strongly retarded in the presence of the first member of the pair, whereas it would occur readily in the presence of the second member. As before, the hydrobromide (sometimes also the hydrochloride) of the chloroaniline having been obtained in ether and the hydrazo-compound added, after 2–3 min the whole mixture is neutralised and oxidised, the quantities of amines formed and of hydrazo-compound remaining then being determined.

Reactions of Hydrochlorides of Hydrazo-Compounds

Hydrazobenzene and 3,3′-dimethylhydrazobenzene hydrochlorides have been tested. Experiments 1 and 6 (Table 2) give for comparison results of the ordinary rearrangement of these hydrazo-compounds in ethereal hydrogen chloride. It is seen that considerable quantities of *oo′*-diamines are

† For reasons which have not been elucidated, 3,4,5-trichloroaniline and also 2,3,5,6-tetrachloroaniline are unsuitable for comparison with hydrazo-compounds.

TABLE 2. Transformation of hydrochlorides of hydrazo-compounds.

Expt. No.	Hydrazo-compound	Solvent	Temp., °C	Atm	Products, %						
					benzidines	biphenylines	oo'-diamines	o-semidines	anilines	azo-cpds.	hydrazo-cpd. reformed
1*	Hydrazobenzene	ether*	—10	N_2	53.4	24.1	7.2	7.0	0.4	0.4	—
2	»	ether	20	N_2	16.2	12.1	—	5.1	16.5	16.8	26.3
3	»	--	20	N_2	13.0	8.1	—	4.1	24.0	24.5	15.6
4	»	—	80	N_2	15.0	11.5	—	5.9	26.2	26.9	7.7
5	»	—	cooling mixture	HCl	38.2	26.6	7.4	18.4	1.0	0.9	—
6*	3,3'-Dimethyl-hydrazobenzene	ether*	—10	N_2	32.6	18.1	16.5	23.0	1.5	1.6	—
7	»	ether	20	N_2	14.2	9.2	—	5.1	24.5	25.2	14.2
8	»	—	20	N_2	15.0	8.5	—	6.5	25.1	25.6	12.2
9	»	—	80	N_2	9.7	6.4	—	8.3	26.8	27.0	13.0
10	»	—	cooling mixture	HCl	27.9	19.0	18.1	20.7	1.6	1.7	—

* Results of the usual rearrangement of hydrazo-compounds in ethereal solution.

obtained besides benzidines, biphenylines, and *o*-semidines. The hydrochlorides of hydrazo-compounds break down after prolonged storage at 20°C in the apparatus in which they had been prepared in ether by treatment of the hydrazo-compound with hydrogen chloride at a 1 : 1 molar ratio. The hydrogen chloride formed by dissociation of the salt gradually brings about rearrangement of part of the salt. It is remarkable that no *oo'*-diamines at all are formed in the absence of a considerable excess of acid. Large quantities of amines and azo-compounds result from the redox reaction

$$2\,[RNH{-}\overset{+}{N}H_2R]\,\overline{Cl} \rightarrow RN{=}NR + 2\,R\overset{+}{N}H_3\,\overline{Cl}$$

which inevitably accompanies the rearrangement. This is revealed when, for example, hydrazobenzene hydrochloride (0.01 mole) reacts with an equimolecular quantity of another suitable compound, e.g. 2,2'-dimethoxyhydrazobenzene in ether. Neither benzidine nor aniline can be detected after such a mixture has been allowed to stand at 0°C for 24 h. The compounds obtained, besides partly regenerated hydrazobenzene and products of the rearrangement of 2,2'-dimethoxyhydrazobenzene, are 2,2'-dimethoxyazobenzene (5.3%), azobenzene (28.8%), and *o*-anisidine (32%). The proceeds by gradual conversion of the 2,2'-dimethoxyhydrazobenzene into the hydrochloride; some of this salt rearranges under the influence of traces of hydrogen chloride, while some of it, being involved in the redox reaction, acts mainly as an oxidant.

Experiments 3, 4, 8, and 9 in Table 2 give results for the breakdown of individual hydrochlorides in a gentle current of dry nitrogen, the apparatus being cooled externally to 20° and heated at 80°C. In expts. 5 and 10 the hydrochlorides were decomposed in an atmosphere of dry hydrogen chloride with external cooling by means of ice and salt. In expt. 4 about half the benzidine was obtained in the form of the monohydrochloride, which was sparingly soluble in water, and this suggested that with rise in temperature hydrazobenzene hydrochloride rearranged without the participation of a second molecule of acid; this would seem to be indicated by the material balance with respect to acid and amino-compounds during the reaction.

However, it was soon shown [18] that hydrochlorides of amino-compounds catalyse the disproportionation of free hydrazo-compounds at elevated temperatures. When, for example, an equimolecular mixture of hydrazobenzene and aniline hydrochloride is heated at 105–110°C for 15 min, disproportionation of the hydrazobenzene reaches 80%; this reaction is catalysed also by weak acids (benzoic, acetic, and butyric acids).

In the mechanism of the reaction very small amounts of hydrogen chloride, resulting from dissociation of the amine hydrochlorides, combine with the hydrazo-compound to form the corresponding hydrochloride, which undergoes a redox reaction. Among the rearrangement products it is possible to detect only traces of *o*-semidines, which are formed by the "thermal" rearrangement of hydrazo-compounds in the absence of acids (see Table 5).

So Called Diacid Salts of Hydrazo-Compounds

Pongratz et al. [19] reported the preparation of hydrazobenzene dihydriodide

$$[C_6H_5\overset{+}{N}H_2 + \overset{+}{N}H_2C_6H_5]I_2^{2-}$$

by the action of a large excess of methyl iodide on hydrazobenzene. A check revealed, however, that the "dihydriodide" could be fractionally crystallised from alcohol, when trimethylphenylammonium iodide (1 mole) and aniline hydriodide (2 moles) were isolated. This product has been synthesised also by the action of a large excess of methyl iodide on aniline [20].

The second diacid salt of hydrazobenzene was the dihydrochloride, Orelkin's "green salt" [17]. When Orelkin's experiment was repeated, a greenish product was obtained which proved to be a mixture of substances resulting from the rearrangement and the disproportionation of hydrazobenzene. Thus later references by Hammond [21] and by Carlin [23] to diacid salts of hydrazo-compounds are devoid of foundation.

Special experiments showed [24] that the formation of appreciable amounts of diacid salts of *N*-methyl-*N'*-phenylhydrazine [25] is excluded in both ethereal and benzene–toluene solutions of hydrogen chloride and hydrogen bromide. Monoprotonated aliphatic–aromatic hydrazines are evidently very weak bases, and double protonation of them is greatly hindered. This must apply even more to the double protonation of considerably more feebly basic substances such as hydrazo-compounds, many of which rearrange very rapidly in weak acids at ordinary temperatures (see Table 1).

3. REARRANGEMENT IN ACID MEDIA

Tables 3 and 4 give results for the rearrangement of hydrazo-compounds in unionised and in ionised acids respectively. The principal representatives selected were hydrazobenzene (I), 2,2'-dimethylhydrazobenzene (II), 3,3'-dimethylhydrazobenzene (III), 4,4'-dimethylhydrazobenzene (IV), 2,2'-dimethoxyhydrazobenzene (V), and 2,2'-diethoxyhydrazobenzene (VI). It is evident from Table 3 that results for the rearrangement differ markedly: in unionised acids the yields of benzidines are not very high; however, far larger quantities of biphenylines are obtained than in ionised acids. A more interesting fact, perhaps, is that with hydrazobenzene and 3,3'-dimethylhydrazobenzene were encounter new substances, *oo'*-diamines, while the quantities of *o*-semidines also increase sharply.

TABLE 3*. Rearrangement in unionised acids.

Expt. No.	Hydrazo-cpd.	Acid	Solvent	Temperature, °C	Products, %					
					benzidines	biphenylines	oo'-diamines	o-semidines	anilines	azo-cpds.
1	(I)	HCl	benz–tol	–10	36.4	29.6	12.8	12.5	0.4	0.4
2	(I)	HCl	—	from –10 to –15	21.7	20.2	17.6	29.0	1.5	1.7
3	(I)	HBr	ether	–10	33.6	30.6	7.5	16.0	1.5	1.6
4	(I)	HBr	—	from –10 to –15	17.7	18.4	10.5	25.5	11.5	1.3
5	(II)	HCl	ether	–10	44.7	25.0	—	1.5	10.5	11.5
6	(II)	HBr	ether	–10	41.1	30.4	—	9.5	6.8	6.0
7	(II)	HBr	—	from –10 to –15	14.5	16.3	—	23.0	21.0	7.0
8	(IV)	HCl	ether	–10	—	—	—	76.1	8.5	8.2
9	(V)	HBr	ether	–10	14.0	18.2	—	18.5	20.0	18.1
10	(VI)	HCl	ether	10–15	48.7	18.8	—	9.2	2.8	2.4

* See also Table 2 (Expts. 1 and 6).

TABLE 4. Rearrangement in ionised acids.

Expt. No.	Hydrazo-cpd.	Alcohol concn., %	Products, %				
			benzidines	biphenylines	o-semidines	anilines	azo-cpds.
1	(I)	99.9	75.5	19.0	2.3	1.3	1.3
2	(I)	95.0	73.0	19.4	2.2	2.3	2.4
3	(I)	95.0	56.5	23.8	2.6	8.1	8.0
4	(I)	85.0	79.0	16.9	1.4	1.1	1.1
5	(I)	75.0	81.2	15.2	1.0	1.1	1.1
6	(I)	60.0	83.2	13.5	0.9	0.9	0.9
7	(I)	45.0	84.3	12.6	0.7	0.9	1.0
8	(II)	95.0	87.0	10.9	0.7	0.5	0.5
9	(III)	95.0	79.2	11.0	3.0	2.0	2.3
10	(IV)	95.0	—	—	58.1	23.0	16.1
11	(V)	99.9	65.7	16.9	2.6	4.7	4.5
12	(VI)	99.9	76.0	8.0	4.4	2.5	2.5

Rearrangement in Unionised Acids[24]

The hydrazo-compound (0.01 mole) is completely dissolved in absolute ether or a mixture of absolute benzene and absolute toluene (benz–tol) in the proportions 2 : 1, and a solution of hydrogen chloride or hydrogen bromide (3–4 moles) in the same solvents is added at between –8° and –10°C. In expt. 10 (Table 3) an ethereal solution of the acid (4 moles) is added at once to a solution of the hydrazo-compound in ether. When solvents are not used, a slow stream of dry hydrogen chloride or hydrogen bromide is passed over the surface of the finely divided hydrazo-compound, the apparatus being gently shaken in a mixture of ice and salt.

The almost colourless aqueous solutions of the reaction products are again shaken with ether, the feebly basic *o*-semidines and azo-compounds being extracted. *o*-Semidines can be determined quantitatively by titration with nitrite.

It is interesting that brominated *o*-semidines—2-amino-4′-bromodiphenylamine and 2-amino-4′-bromo-2′,3-dimethyldiphenylamine—are formed by the action of dry hydrogen bromide on crystalline hydrazobenzene and 2,2′-dimethylhydrazobenzene. Large quantities of aniline (expt. 4) and of *o*-toluidine (expt. 7) are also obtained. These substances result from a secondary reaction: the hydrobromides of the hydrazo-compounds which are formed are reduced by hydrogen bromide to anilines with simultaneous bromination of the substances—the *o*-semidines—which are most readily brominated in the reaction mixtures. Benzidine is reprecipitated as the sulphate; other benzidines are salted out from strongly acidified solutions and purified. The filtrates are used to determine anilines, which are volatile in steam, *oo*′-diamines, and biphenylines; these last are easily separated after conversion into the dibenzoyl derivatives, by means of their differing solubilities in alcohol and in ether.

Rearrangement in Ionised Acids[26,27]

The process is conducted in aqueous–alcoholic solutions of hydrogen chloride; in some experiments anhydrous alcohol is used. A solution of hydrazobenzene (0.01 mole) in alcohol, which has been strongly cooled under nitrogen, is at once mixed with a solution of hydrogen chloride (0.1 mole), the total volume being 100 ml and the temperature ~ 0°C. After 2 h crystals of benzidine hydrochloride are separated and are converted into the sulphate. The alcohol is evaporated off at 10–20°C. The residue is diluted with water, the major portion of the acid is carefully neutralised, and the *o*-semidine and azobenzene are completely extracted with ether. The aqueous portion contains traces of benzidine, biphenyline, and aniline. The benzidine having been separated, the total biphenyline plus aniline is determined by diazotisation, the quantity of aniline being found after repeated distillation in steam. In expt. 3 (Table 3) (I) is added to the acid at 45–50°C during 15 min. Compounds (II) and (IV)–(VI) are added steadily to a solution of hydrogen chloride (0.1 mole) in alcohol (100 ml) at 0°C steadily over 30 min. After $1\frac{1}{2}$ h the reaction mixtures are treated as in the directions just given for (I), and also for rearrangement in unionised acids.

In part of the analysis investigators are usually guided by the data of Carlin et al.[28] (who employed a spectrophotometric method), according to which hydrazobenzene is completely converted, over a wide range of conditions in 95% ethanol, into a mixture of benzidine and biphenyline in the proportions 70 : 30. Actually, we have seen (Table 4) that the ratio of benzidine to biphenyline differs from the values obtained by Carlin, and moreover is closely connected with the alcohol concentration: in 95%, 75%, and 45% ethanol the proportions are respectively 79 : 21, 84 : 16, and 87 : 13 (compared with 92.8 in aqueous hydrochloric acid). With rise in temperature the quantity of benzidine diminishes appreciably relative to biphenyline and other substances, among which is *o*-aminodiphenylamine. Finally, the amounts of disproportionation product increase greatly with rise in temperature.

With regard to other hydrazo-compounds, according to Carlin and Odioso[22] the rearrangement of 2,2′- and 3,3′-dimethylhydrazobenzenes yields solely the corresponding benzidines‡. But it is well known in industry that, even under special conditions, secondary products are inevitably obtained together with *o*-tolidine. In alcoholic medium with hydrogen chloride (Table 4, expt. 8), however, ~ 11% of 3,3′-dimethylbiphenyl-2,4′-diamine is obtained. In the case of 3,3′-dimethylhydrazobenzene (Table 4, expt. 9) 11% of 2′,4-dimethylbiphenyl-2,4′-diamine and 3% of 2-amino-3′,4-dimethyldiphenylamine are obtained.

Ingold and Kidd[30] considered the intramolecular character of the rearrangement to be proved by the melting-point

‡ The same error has been made in a recent paper by Ingold and his coworkers[29], who consider that *o*-tolidine is obtained uncontaminated with its isomers.

diagrams of the mixtures of substances formed by the simultaneous rearrangement of 2,2'-dimethoxy- and 2,2'-diethoxy-hydrazobenzenes: according to their results the only substances obtained besides disproportionation products are pure 3,3'-dimethoxy- and 3,3'-diethoxy-benzidines, moreover in identical yield (73%). Actually, however, under Ingold and Kidd's conditions the yields in anhydrous ethanol are ~66% of 3,3'-dimethoxybenzidine (expt. 11) and 76% of 3,3'-diethoxybenzidine (expt. 12). Besides dianisidine ~ 20% of isomers are obtained, and in the case of diphenetidine up to 12% of isomers, which can be separated without loss of the main substances only by special acid purification.

Determinations by the Reviewer[24] indicate that hydrazobenzene rearranges more rapidly in ethereal than in 95%-ethanolic solutions of hydrogen chloride by factors of 30–40, and the rate of rearrangement in 99.9% ethanol exceeds that in 95% ethanol by a factor of ~ 150. The rates are incomparably higher in benzene–toluene solutions of hydrogen chloride than in ethereal solutions.

2,2'-Dimethylhydrazobenzene rearranges more rapidly than hydrazobenzene itself in ethereal solutions of hydrogen chloride by factors of ~ 1000, but more rapidly than in solutions of hydrogen chloride in 95% ethanol by a factor of only 4. Rates of rearrangement in ethereal and benzene–toluene solutions of hydrogen bromide exceed the rates in hydrogen chloride by factors of 10^5, results being comparable only in ethereal or in the benzene–toluene solutions.

In 95% ethanol hydrazobenzene rearranges at almost the same rate with hydrogen chloride and with hydrogen bromide. 2,2'-Dimethylhydrazobenzene rearranges twice as fast with hydrogen bromide as with hydrogen chloride.

Mechanism of the Rearrangement of Hydrazo-Compounds in the Presence of Acids

Not long ago almost all research workers considered that the rate of rearrangement in ionised acids was directly proportional to the first power of the concentration of the hydrazo-compound and the square of the concentration of protons[31]. The Reviewer published a paper opposing this hypothesis[26], and the protagonists of this theory found themselves compelled to re-examine their positions[32–37].

Hydrazo-compounds are unsuitable for important kinetic investigations, since their resemblance to diacid bases of the usual type is purely formal: although the rate of monoprotonation depends on the basic strength of the initial hydrazo-compound, the rate of the ensuing stage is related only indirectly to the basic strength of the monoprotonated molecule, being determined by a different property of the latter, its *stability in the presence of the acidic agent*. If the difference between the rates of the first and second stages is considerable, the illusion is created of a double protonation, which occurs with compounds capable of forming salts which are relatively stable to the further action of the acid (Table 1). In several cases (Table 1, expts. 13, 16, 17, 19, 20, and 22–25), however, the monoprotonated hydrazo-compounds are extremely unstable to acids: in other words, the rate of the second stage is very high. This simple fact becomes obvious from a knowledge of the salts of hydrazo-compounds; it proves the occurrence of a "spontaneous" rearrangement of monoprotonated hydrazo-compounds.

In the presence of acids rearrangement is invariably stepwise: the monoprotonated molecule which is formed rearranges *only under the further influence of the acid*. The very great difference between the results obtained in unionised and in ionised acids is probably due primarily to fundamental differences in the transition states produced. The reaction of crystalline hydrazo-compounds with hydrogen chloride or hydrogen bromide is apparently most characteristic of the former case. The process occurs in the solid phase, and can be represented as

$$[RNH—\overset{+}{N}H_2R]\,\bar{X} + H \rightleftarrows [RNH—\overset{+}{N}H_2R]\,X \ldots HX \rightarrow \text{Rearranged product}.$$

The presence of solvents has a fundamental influence: they change the strength of acids, and may to some extent dissolve the salts of hydrazo-compounds, with the result that rearrangement takes place partly in solution. Finally, the nature of the acid may very likely have an effect, as follows from a comparison of the results obtained with hydrogen chloride and with hydrogen bromide.

While disagreeing with the hypothesis of a spontaneous partial rearrangement put forward by Blackadder and Hinshelwood, the Reviewer considers that they have made a useful contribution in suggesting that in ionised acids a monoprotonated hydrazo-compound rearranges on the approach of a proton[37]. The transition state in aqueous and aqueous–alcoholic solutions can be written

$$RNH—\overset{+}{N}H_2R \quad H_3\overset{+}{O}.$$

In anhydrous alcohol the reaction is catalysed by the ethyloxonium ion. It is significant that, although the rate of the reaction is greater in 99.9% than in 95% ethanol by a factor of approximately 150, the results for the rearrangement of hydrazobenzene are almost the same (Table 4, expt. 1). And yet the results are affected by the nature of the solvent and of the acid. We have already seen that, when alcohol is diluted with water, the ratio of benzidine to biphenyline is increased. This ratio in 95% alcohol (87 : 13) is appreciably increased also by replacing hydrochloric with sulphuric acid. This may be linked with a specific effect of the unionised acid on the monoprotonated hydrazo-compound, which is probable also with rearrangement in weak acids.

From Table 1 it is possible to obtain a rough idea of the relative rates of rearrangement of a series of hydrazo-compounds, and also to find further support for the ideas on the mechanism of rearrangement. Acetic acid (95%) was used.

The rates of rearrangement of many hydrazo-compounds differ so greatly that it is not possible to express them on the same scale. In several cases, therefore, dioxan was added to slow down the rearrangement. This resulted in a marked diminution in the reaction velocity: thus in 95% acetic acid the conversion of hydrazobenzene reaches 50.5% after 3 h, whereas when 8 ml of dioxan has been added a period of 800 h is required for the transformation to attain 68%; with 2,2'-dimethylhydrazobenzene a time of 8 min produces a change of 42.5%, but on the addition of dioxan 24 h will yield 62%.

The examples of hydrazonaphthalenes selected by Banthorpe, Hughes, and Ingold were an unhappy choice for ascertaining the true nature of the rearrangement. Because of the extreme instability of the monoprotonated hydrazo-compounds, the rates of the first and second stages differ little, and it is extremely difficult to divide the rearrangement into stages, the whole process occurring very rapidly (expts. 23–25). And yet, in contrast to

these workers' results, salts of 1,1'- and 1,2'-hydrazonaphthalenes can be detected in dioxan diluted with ether, as has been stated in the Section on the salts of hydrazo-compounds.

2,2'-Diethoxy- and 2,2'-dimethoxy-hydrazobenzenes (expts. 20 and 17) can usefully be contrasted with 1,1'- and 1,2'-hydrazonaphthalenes. Their rates of rearrangement are close to those for the hydrazonaphthalenes, and there can hardly be any doubt that the "kinetic order with respect to the acid" will not differ significantly from 1.0 here. But the example of 2,2'-diethoxyhydrazobenzene clearly reveals the presence of two stages in the rearrangement: the hydrochloride of the hydrazo-compound can be isolated in 60–65% yield (Table 1, expt. 20), obviously owing to the coarse-grained character of the precipitate in ether. In spite of a lower rate of rearrangement, the quantity of 2,2'-dimethoxyhydrazobenzene hydrochloride which can be isolated does not exceed 10% (see Table 1, expt. 17).

4,4'-Dimethoxy- and 4,4'-diethoxy-hydrazobenzenes are very interesting (expts. 19 and 22). Their rates of conversion in acids are especially high, ~ 80% of disproportionation products being formed, whereas the maximum quantity of *o*-semidines which can be isolated under special conditions does not exceed 10%. Clearly, there is no possibility of recovering intermediate products, but nevertheless the stepwise character of the whole process is demonstrated perfectly by these examples: as has been stated repeatedly, disproportionation products result from a secondary reaction, the interaction of two molecules of the monoprotonated hydrazo-compound. The figures given (80% and 10%) indicate that the rate of this bimolecular reaction considerably exceeds the rate of conversion of the monoprotonated hydrazo-compound into the *o*-semidine.

Remarks on the Rearrangement of 4,4'-Substituted Hydrazobenzenes

An increasing number of attempts have been made recently to establish by kinetic methods the mechanism of the rearrangement of 4,4'-substituted hydrazobenzenes. Carlin and Wich[23] found that the rearrangement of 4,4'-dimethylhydrazobenzene is of the second order with respect to the acid: the reaction products were *o*-semidine, *p*-toluidine, and *p*-azotoluene in the proportions 40 : 40 : 20. It has already been mentioned that in reality the proportions of these products are different—58 : 23 : 16 (Table 4, expt. 10)—the slight predominance of toluidine over azotoluene being explained, in the Reviewer's opinion, by the reducing action of alcohol on the monoprotonated molecule of the hydrazo-compound.

Dewar and McNicoll[38] obtained values of 1.58 and 1.51 for the kinetic order with respect to the acid in the cases of 4-chloro-4'-methylhydrazobenzene and 4-chloro-4'-t-butylhydrazobenzene respectively, but they did not ascertain the composition of the products of the rearrangement. The results obtained by the Reviewer indicate the proportions of *o*-semidine, anilines, and azo-compound to be 24 : 33.5 : 35.5 in the former case, and 38 : 25 : 28 in the latter case.

Shine and his coworkers[39,40] studied the rearrangement of 4,4'-di-t-butylhydrazobenzene and 4,4'-divinylhydrazobenzene; in the former case 45–54% of the hydrazo-compound underwent rearrangement, and 48–50% disproportionation. In the latter case the order of the reaction with respect to acid was found to be 1.0, but the products resulting from the interaction of the divinylhydrazobenzene and hydrogen chloride in ethanol remained unknown: in any case, they were stated to be neither a semidine nor disproportionation products. From what has been stated the authors' view cannot be accepted that a "benzidine rearrangement" is taking place here.

Thus in the course of the rearrangement of 4,4'-substituted hydrazobenzenes the monoprotonation of the hydrazo-compound is followed by two parallel reactions—rearrangement of the monoprotonated hydrazo-compound to an *o*-semidine, and interaction of the latter two monoprotonated molecules to give anilines and azo-compounds.

4. "THERMAL" REARRANGEMENT OF HYDRAZO-COMPOUNDS

Meisenheimer and Witte[41] discovered that, when 2,2'-azonaphthalene dissolved in alcoholic alkali is boiled with zinc dust, 1,1'-binaphthyl-2,2'-diamine is formed. These workers, and subsequently also Jacobson[12], interpreted this phenomenon as a rearrangement under the influence of the alkali, but it has been shown[16] that it is not the alkali but the heating which leads to rearrangement both of 2,2'- and of 1,1'-hydrazonaphthalene.

A few years later the products of the rearrangement were determined, though only qualitatively, by Večeřa et al.[42] as a result of the very prolonged heating (at 150°C) of hydrazobenzene and 2,2'-dimethylhydrazobenzene (as well as of 4-methylhydrazobenzene and 1,1'-hydrazonaphthalene). Almost at the same time the "thermal" rearrangement of 2,2'-hydrazonaphthalene was studied by Shine[43], who obtained satisfactory results after only a few years[44]. With regard to 1,1'-hydrazonaphthalene, the author himself admits that this case proved to be too difficult for him.

When studying the "thermal" rearrangement is is important to establish the optimum temperature conditions. Overheating leads to copious tar formation, which probably occurred in Večeřa's experiments.

Rearrangement of Hydrazo-Compounds of the Benzene Series

The compounds which the Reviewer has tested can be divided into two groups: the first comprises hydrazo-compounds which form disproportionation products almost exclusively, this group including 4-chloro-, 4-bromo-, and 4,4'-dichloro-hydrazobenzenes; the second group contains the principal hydrazo-compounds (Table 5). Heating was conducted in an atmosphere of nitrogen in sealed tubes. Products of rearrangement are formed as well as products of disproportionation, their quantity sometimes exceeding 25%. They are *o*- and *p*-semidines, with one or other isomer predominating in individual cases. 4-Methylhydrazobenzene gives not only 2-amino-5-methyldiphenylamine but also a second possible isomer—2-amino-4'-methyldiphenylamine—which had not been observed by Jacobson[45] in the acid rearrangement, and was not detected in Večeřa's "thermal" rearrangement[42].

In several cases considerable quantities of *p*-semidines appear, which are not formed at all in the rearrangement of the same hydrazo-compounds in acid media. Benzidines and biphenylines could not be detected in any appreciable quantities.

TABLE 5. "Thermal" rearrangement in the benzene series.

Substituted hydrazobenzene	Temp., °C	Duration of heating, h	Products, %			
			o-semidines	p-semidines	anilines	azo-cpds.
Hydrazobenzene	140—145	120	16.7	12.5	31.5	33.4
4-Chloro-	140—145	20	—	—	45.2	47.5
4-Bromo-	110	16	—	—	46.5	50.3
4-Methyl-	140—145	116	18.6	8.1	33.5	35.6
2,2′-Dimethyl-	140—145	120	8.3	13.1	36.0	38.0
3,3′-Dimethyl-	140	100	32.0	8.2	26.2	29.1
4,4′-Dimethyl-	140—145	100	15.5	—	38.0	38.2
2,2′-Dimethoxy-	120—125	26	16.0	9.2	28.5	40.2

Rearrangement of Hydrazo-Compounds of the Naphthalene Series—Influence of Solvents

Hydrazonaphthalenes are worthy of special attention in the study of the "thermal" rearrangement. The composition of the final products varies greatly depending on factors which have hardly any effect on the rearrangement of hydrazo-compounds of the benzene series. Attention has been paid mainly to the more complicated but also more interesting rearrangement of the 1,1′-isomer[46,47]. The rate of rearrangement is considerably greater in alcohols, ethylene glycol, and formamide than in other solvents. In ethanol at 100°C some 87% of the dissolved 1,1′-hydrazonaphthalene has decomposed after only 10 min, the corresponding proportions of the 1,2′- and 2,2′-isomers being 53% and 27% respectively; the rates are still higher in formamide. In benzene 52%, 11%, and 3.5% are obtained respectively, in acetonitrile 45%, 8%, and 3.5%, and in pyridine 23.5%, 3.4%, and 1.0% of transformed hydrazo-compounds. However, a far more important fact is that the quantitative composition of the rearrangement products is often linked with the nature of the solvent. These products can be divided into two groups according to the mechanism of their formation, which will be discussed below. The first group comprises *o*- and *p*-diamines and the 2,2′-binaphthyl-1,1′-imine [dibenzocarbazole] corresponding to the *o*-diamine; the second group comprises the *o*- and *p*-semidines. In weakly polar solvents (cyclohexane, benzene, toluene, 1,4-dioxan) the quantities of semidines sometimes exceed 50% of the total rearrangement products. The quantity of semidines diminishes with increasing polarity of the solvent. The addition to weakly polar solvents of water, having a high dielectric constant, may result in a considerable decrease in the yields of semidines; this occurs in benzene and in dioxan, but water has far less effect in experiments with ethanol and with pyridine.

It is interesting to trace the influence of solvents on the relative proportions of 1,1′- and 4,4′-diamines. The ratio of 1,1′- to 4,4′-diamine is usually 0.67, the latter being obtained as the formyl derivative, whereas the less basic 1,1′-diamine is obtained in the free state§.

The quantities of dibenzocarbazole also depend sometimes on the nature of the solvent: far more is obtained in hydrocarbons and alcohols, in amounts exceeding those of the 1,1′-diamine by factors of 3–4; in pyridine, however, the yields of the dibenzocarbazole are very low, only ~ 20% of those of the *oo*′-diamine.

§ There appears to be an omission in the Russian text, since there is no reference to the solvent in this sentence (Ed. of Translation).

Rearrangement in alcoholic alkali gives very interesting results for all three isomeric dibenzocarbazoles. In anhydrous methanol and ethanol ~ 25% of dibenzo[*ai*]-carbazole is obtained, together with more than 50% of the [*ag*] isomer and ~ 20% of the 2,2′-dinaphthylamine. If, however, metallic sodium has first been dissolved in dehydrated alcohol to obtain a 0.1 *N* solution of the alkoxide, rearrangement is just as rapid, but it is remarkable that no dibenzocarbazoles are formed at all.

Results for the rearrangement of 1,2′- and 2,2′-hydrazonaphthalenes are simpler[47]. The former isomer yields an *oo*′-diamine, a dibenzocarbazole, and 4-amino-1,2′-dinaphthylamine; disproportionation is insignificant. Just as with 1,1′-hydrazonaphthalene, very considerable quantities of the *p*-semidine are obtained in benzene and in dioxan; the semidine is almost completely absent in alcohols. Only the *oo*′-diamine and the dibenzocarbazole are formed from 2,2′-hydrazonaphthalene.

In view of the above observations on the influence of the solvent on the rearrangement, it seems possible that the molecules undergoing rearrangement may interact with the solvent molecules not only before but also during the reaction. Thus the solvent, by tending to increase the lability of the hydrazo-compound, facilitates the initial stage in the process and also influences the composition of the final products.

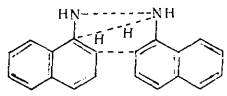
If rearrangement is difficult, *o*- and *p*-semidines are obtained; this occurs in the benzene series, and also in several cases with 1,1′- and 1,2′-hydrazonaphthalenes. In agreement with Večeřa's hypothesis[42] it is very likely that the formation of semidines results from the interaction of radicals produced by cleavage of the HN—NH bond in the hydrazo-compound. It must be added, however, that such a radical reaction should be associated with conditions consistent with our views on the rearrangement as an intramolecular process: in other words, either this is an intramolecular radical reaction[48] or, if the radicals are kinetically independent, their lifetime is extraordinarily brief.

Solvents having well defined polarity facilitate the rearrangement, resulting in a considerable diminution in the

TABLE 6. "Thermal" rearrangement of 1,1′-hydrazonaphthalene.

Solvent	ml	Duration of reaction, h	Products, %							Semidines total products %
			1,1′-diamine	dibenzocarbazole	4,4′-diamine	o-semidine	p-semidine	naphthylamine	azonaphthalene	
—	—	12	6.6	25.0	20.5	8.4	23.4	5.0	2.3	37.9
Cyclohexane	25	6.5	4.7	13.5	9.8	12.9	24.9	15.2	11.0	57.4
Benzene (abs.)	20	6.0	3.4	14.1	8.3	10.2	20.0	19.8	17.1	53.9
Benzene + H_2O	20	6.0	5.1	18.6	11.1	8.8	12.6	18.0	17.3	38.1
Toluene	20	6.0	4.7	16.9	12.2	10.2	11.8	18.8	16.0	39.4
Dioxan (abs.)	15	3.0	5.2	12.7	7.3	10.8	20.3	18.4	15.1	55.2
Dioxan + H_2O	13.5 1.5	3.0	12.7	12.1	18.0	8.7	14.1	14.0	9.5	34.8
Methanol	15	2.0	5.8	25.0	25.4	7.1	5.8	14.8	9.1	18.7
Methanol + Na	15	1.5	25.2	—	24.8	7.1	8.9	15.1	10.0	24.2
Ethanol	15	1.5	8.7	25.0	15.5	7.6	12.1	15.4	9.5	28.6
85% Ethanol	15	1.5	8.8	25.4	18.0	7.1	8.8	13.2	8.3	23.3
Ethanol + Na	15	1.0	33.7	—	24.4	7.0	4.7	13.0	9.2	16.8
Pyridine	10	4.0	23.2	4.0	17.2	7.5	8.3	18.5	13.5	26.6
Pyridine + H_2O	7.5 2.5	4.0	26.1	5.8	25.0	6.6	7.4	14.2	7.2	19.7
Ethylene glycol	15	2.0	10.7	39.4	24.1	1.1	9.0	7.2	1.8	12.0
Acetone	10	3.0	4.3	13.5	14.1	1.8	11.4	22.2	18.3	29.3
Acetonitrile	15	2.5	5.2	18.0	18.6	5.4	4.1	21.0	17.9	18.5
Formamide	15	3.0	21.4	16.0	52.6	—	—	—	1.1	0
Formamide – NH_4OH	14 1	2.5	40.4	11.2	33.5	traces		4.2	2.1	0
Formamide + pyridine + NH_4OH	6 4 1	2.0	36.7	8.6	30.0	1.0	1.8	8.5	5.1	3.6

quantities of semidines from 1,1′- and 1,2′-hydrazonaphthalenes and a corresponding increase in the yields of diamines and dibenzocarbazoles. It is very significant that none of the three isomeric dibenzocarbazoles, which are sometimes formed in very large quantities, can be obtained from the binaphthyldiamines, since this would require more severe conditions [16]. This has been verified with all three isomers. Hence they must be formed at the instant of rearrangement. A conceivable transition state is



when the bond between the nitrogen atoms is not finally broken, and nor are new bonds finally established.

Azo-compounds and anilines are formed by an intermolecular redox reaction. In the benzene series, where rearrangement is greatly hindered, predominantly disproportionation products are obtained; but in the naphthalene series disproportionation occurs mainly in the case of 1,1′-hydrazonaphthalene, where rearrangement goes far more easily than with the 1,2′- and 2,2′-isomers. It is obvious that the redox reaction also goes very rapidly with 1,1′-hydrazonaphthalene. A striking feature is that usually the quantity of naphthylamine considerably exceeds that of 1,1′-azonaphthalene, especially with alcohols, ethylene glycol, aqueous pyridine, and aqueous dioxan. It is very likely that in these solvents we must reckon with water and alcohols exerting a reducing action on 1,1′-hydrazonaphthalene.

In conclusion it must be noted that the exceptional instability of certain hydrazo-compounds permits their rearrangement to be accomplished at ordinary temperatures. Thus 1,1′-hydrazonaphthalene dissolved in a mixture of formamide and pyridine, for example, is completely decomposed after 3 weeks, 50% of the *oo′*-diamine, 2% of the dibenzocarbazole, 40% of the *pp′*-diamine, and ~ 2% of the azo-compound being obtained. The breakdown of 1,2′-hydrazonaphthalene in a mixture of formamide and pyridine is somewhat slower, ~ 80% of the *oo′*-diamine being obtained together with small quantities of the dibenzocarbazole and the azo-compound. 2,2′-Hydrazonaphthalene decomposes far more slowly: after extremely prolonged storage under freshly boiled alcohol filling the whole apparatus, ~ 16% of pure 1,1′-binaphthyl-2,2′-diamine was formed together with a large quantity of an azo-compound. 4,4′-Dimethoxy- and 4,4′-diethoxy-hydrazobenzenes decompose very rapidly in a mixture of pyridine and formamide: no hydrazo-compound remained in the reaction mixtures after only a few days. They were oxidised mainly to azo-compounds (45–50%); in addition, 25–30% of the corresponding arylhydroxylamines and small quantities of anilines were formed. In other solvents the decomposition of hydrazo-compounds takes place more slowly. For example, 4,4′-dimethoxyhydrazobenzene in a solution of dioxan and methanol disappears completely after storage for 1 month, ~ 50% of an azo-compound, 25% of the arylhydroxylamine, and 8% of the aniline being obtained.

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POLYCARBORANES

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Great progress has recently been made with polymers containing boron, and several reviews of this work have appeared[1-5]. The polymer chemistry of boron has recently been enriched with a new class of compounds—the so-called polycarboranes.

Carboranes—products of the reaction between decaborane and acetylenic compounds—are obtained via the intermediate product in the interaction of decaborane with Lewis bases (nitriles, amines, amides, isocyanates), with subsequent displacement of the base by the action of acetylene and its derivatives:

$$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2B_{10}H_{12} + H_2$$

$$(CH_3CN)_2B_{10}H_{12} + RC{\equiv}CR' \longrightarrow RC\!-\!CR' + 2CH_3CN + H_2 .$$

The formation of carborane derivatives was described simultaneously by Soviet[6,7] and by American[8-18] research workers.

X-Ray examination as well as theoretical calculations of possible structures of several carboranes[19-25] suggest that a system of ten boron atoms is combined with two carbon atoms to form an icosahedron in which the C–C σ-bond is oriented at right angles to the plane of the 6,2,4,9-positions of the boron atoms in the decaborane unit (Fig. 1). In conformity with the recommendation of the Committee on Nomenclature of the Division of Inorganic Chemistry of the American Chemical Society[26] the name "carboranes" is used to denote compounds containing the system



in which the carbon atoms are regarded as heteroatoms and are numbered 1 and 2.

When carborane is heated above 475°C [18] it isomerises into a new compound, which has been termed "neocarborane". It is assumed that the thermal isomerisation involves transformation of the icosahedral structure with a strained C–C bond into the stable regular structure of neocarborane, which is free from strain. In such an icosahedral structure the carbon atoms are completely analogous to the boron atoms, and form three-centre bonds

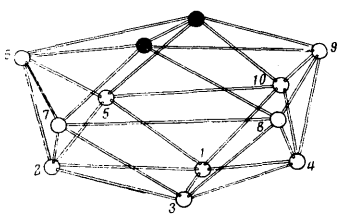


Fig. 1. Structure of the carborane molecule.

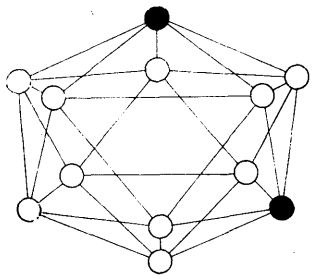


Fig. 2. Structure of the neocarborane molecule.

with the nearest boron atoms (Fig. 2). Neocarboranes resemble carboranes in their properties. However, the infrared spectra differ markedly (Fig. 3), as also certain physical and chemical properties (lower polarity, lower melting points, inability to form cyclic compounds, etc.).

Comparison of the infrared spectra of neocarborane and carborane reveals considerable differences in the range 1250–900 cm^{-1}. The high peak at 1212 cm^{-1} characteristic of carborane is completely absent from the spectrum of neocarborane. The bands in the region of 1149, 1043, 1015, and 995 cm^{-1}, which are characteristic of carborane, disappear from the spectrum of neocarborane, and new bands appear in the region of 1158, 1069, 1022, and 991 cm^{-1}.

Carborane derivatives can be prepared both from acetylenic compounds and also by converting some carborane derivatives into others. A series of monomers have been obtained based on carboranes (diols, dicarboranic acids, dichlorides, diesters, di-isocyanates, vinyl derivatives, acrylates, epoxides, silanes, etc.), which are used for the preparation of various carborane polymers[9,11,12,14-17].

The present paper describes methods for obtaining various polymers of carborane, and also their properties.

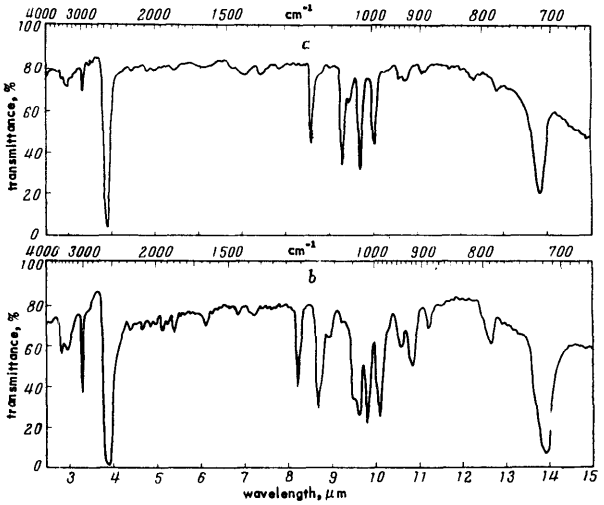
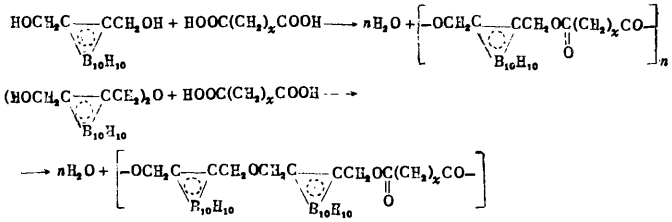


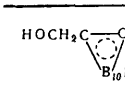
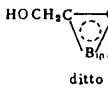
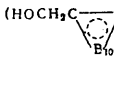
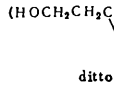
Fig. 3. Infrared spectra of: *a*) neocarborane; *b*) carborane.

Among the polymers of carborane which have been described, the polyesters are widely represented in the literature[27-29]. Numerous carborane derivatives[27]—diols, acids, acid chlorides, esters—have been used for the synthesis of polyesters. The latter has been accomplished by the polycondensation of organic and fluorinated organic diols of carborane with dibasic acids or with their chlorides. Polyesters of molecular weight 2000–3000 have been prepared by the polycondensation of carboranediols with various dicarboxylic acids or chlorides:



The polymers obtained and their properties are listed in Table 1.

TABLE 1. Properties of carborane polyesters.

Diol	Dibasic acid	Properties of polyesters		Ref.
		M*	m.p., °C	
	HOOC—COOH	1160	brittle, softens at 72–74°C	29
ditto	HOOC—CH_2—COOH	1530	brittle, softens at 63–66°C	29
»	HOOC—$(CH_2)_2$·COOH	2600	brittle, flows at 90–91°C	28
»	$HOOC(CH_2)_3COOH$	3600	flows at 63°C	27
»	ditto	3600	plastic, flows at 78°C	28
»	$HOOC(CH_2)_4COOH$	2650	flows at 66°C	28
»	ditto	3000	plastic, flows at 81°C	27
»	$HOOC(CH_2)_7COOH$	2300	viscous liquid (88 P) at 100°C	28
»	ditto	3200	flows at 22°C	27
»	$HOOC(CH_2)_8COOH$	2400	viscous liquid (78 P) at 100°C	27
»	ditto	3200	flows at 28°C	28
»	$ClOC(CH_2)_2COCl$	1907	vitreous substance	27
»	$ClOC(CH_2)_4COCl$	2040	amber-coloured plastic	27
	$ClOCC_6H_4COCl$	—	brittle, softens at 270°C	27
	$HOOC(CF_2)_2COOH$	2500	61°C	28
ditto	$HOOC(CF_2)_3COOH$	3000	50°C	28
	$HOOC(CF_2)_4COOH$	3400	55°C	28
»	$ClOC(CF_2)_3COCl$	2540	plastic, flows at 57°C	27
	$ClOC(CF_2)_3COCl$	960	brittle, melts at 200°C	27
	$ClOC(CF_2)_8COCl$	1600	softens at 74°C	27
				
ditto	$HOOC(CH_2)_2COOH$	2800	hard, brittle, softens at 90°C	27
»	$ClOC(CH_2)_4COCl$		hard, brittle, flows at 70°C	27
»	$HOOC(CH_2)_8COOH$		brittle, 200 P at 100°C	27

* Molecular weight determined by cryoscopic or precision ebullioscopic methods.

Inspection of the melting points of the carborane polyesters has revealed (though not very clearly, because of the incompleteness of the homologous series) the "evenness factor" discovered by Korshak and Vinogradova[30], consisting in the fact that polyesters of polymethylenedicarboranic acids having an odd number of carbon atoms melt at lower temperatures than both compounds of the polyester having an even number of carbon atoms in the molecule. This phenomenon is explained by polar effects in the dicarboxylic acid and diol molecules.

Examination of Table 1 shows that the replacement of CH_2 by CF_2 groups also lowers the softening point of a carborane polyester.

The carborane group consists of a sphere of effective van der Waals radius 4 Å. It is strongly electrophilic. Difficulties arising in the synthesis of the polymers and the properties of the products are determined both by steric and by electronic factors.

The effect of the carborane group on the properties of the polymers was studied on the polyadipates[31] obtained by the polycondensation of adipic acid with 1,2-bishydroxymethylcarborane, butane-1,4-diol, and butyne-1,4-diol. The first of these products was a viscous liquid, exhibiting no tendency to crystallise. The analogous organic polymers of equivalent molecular weight were crystalline waxes. Hence it can be concluded that the carborane group impedes the dense packing of the molecules and the subsequent crystallisation of the polymer. Investigations have shown[27] that the polyesterification of carboranediols proceeds considerably more slowly than that of organic diols. Thus a polyadipate of molecular weight 2500 can be obtained from butane-1,4-diol and adipic acid in 24 h, whereas synthesis of a poly(carborane adipate) at the same temperature lasts 5 days. This is indicated also by the fairly low rate constants given in Table 2 for the formation of a poly(carborane adipate)[32].

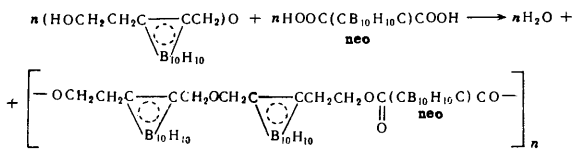
If both diol and dicarboxylic acid contain a carborane group, the adverse effect of the two carborane groups is so great that either no polymeric compound is obtained at all or else the resulting polymer has a low molecular weight.

It is possible that increasing the distance between the carborane system and the functional groups of the molecule will tend to diminish the influence of the steric factor of the carborane unit. Table 1 shows that, when bishydroxymethylcarborane is replaced by bis-(2-hydroxymethylcarboran-1-ylmethyl) ether, which contains two carborane groups, the molecular weight of the product decreases from 2500 to 960. When, however, bis-(2-hydroxyethylcarboran-1-ylmethyl) ether is used, i.e. when the distance between the carborane nucleus and the hydroxyls in the molecule is increased, the molecular weight of the compounds is somewhat higher (1600 instead of 960).

TABLE 2. Rate constants of the formation of carborane adipate polyester.

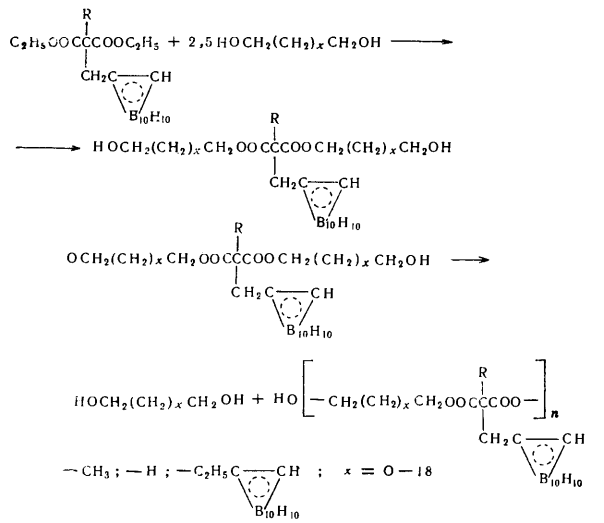
Temp., °C	Rate constant, mole g^{-1} min^{-1}
170	$7.46 \cdot 10^{-4}$
190	$1.59 \cdot 10^{-3}$
205	$2.48 \cdot 10^{-3}$

Interaction of bis-(2-hydroxyethylcarboran-1-ylmethyl) ether with neocarboranedicarboxylic acid according to the equation



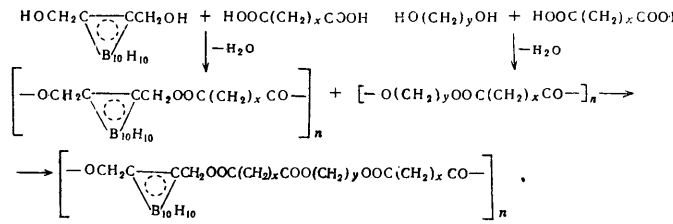
yields vitreous polymers of molecular weight 1730 and softening point 125°C. The resulting neocarborane polyesters are more crystalline than the carborane polymers, probably as a consequence of more compact packing of the molecules.

The steric and inductive effects of carborane groups which inhibit polymerisation may be exhibited when these groups are present in the side-chain. Thus polycarboranemalonates can be obtained by the esterification of carboranemalonates with glycols[27]. The process involves formation of an intermediate addition product of the diol and the carborane diester, followed by its self-condensation to a linear polymer accompanied by elimination of the glycol:



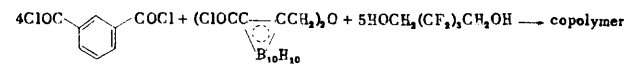
The products are vitreous materials of relatively low molecular weight. Attempts to increase the molecular weight were unsuccessful even when solvents of high boiling point were used and the molar ratio of the reactants was varied.

To obtain polymeric compounds having lower softening points and pour points, ternary copolymers were synthesised from bishydroxymethylcarborane, diethylene glycol, and dicarboxylic acids[28]. The mixed carborane polyesters were prepared by first synthesising polyesters of low molecular weight by the interaction of bishydroxymethylcarborane and a polymethylenedicarboxylic acid (adipic or glutaric acid), and also of diethylene glycol with the dicarboxylic acid, and then bringing about polyesterification between the two polyesters of low molecular weight to yield the mixed carborane polyester of higher molecular weight:



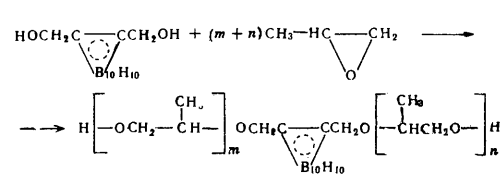
The copolymers were liquids of viscosity 33–35 P and molecular weight 2000–2200.

Ternary copolymers have been synthesised[27] from terephthaloyl and carboranedicarbonyl chlorides and a fluorocarbon diol:



The molecular weight of the product is 2500. The polymer softens at 35°C, possesses elastic properties over the range 35–56°C, and is converted above 56°C into a sticky liquid. The molecular weight of another copolymer obtained also from terephthaloyl chloride, together with 1,2-bishydroxymethylcarborane and hexafluoropentanediol, is 3300.

Oligomeric compounds having low softening points and pour points have been obtained by the migration copolymerisation of bishydroxymethylcarborane with alkyloxirans[33]. The migration copolymerisation of the former component with propylene oxide at 75–100°C and 3–5 atm yields a polyoxypropylenecarboranediol which is a liquid of viscosity 22 P comprising 5–6 structural units:



Fractionation of the polymer by adsorption chromatography[34] showed it to be polydisperse with a mean molecular weight of 500.

Attempts to increase the molecular weight of the polymer by varying the temperature of the synthesis or increasing the molar ratio of propylene oxide to bishydroxymethylcarborane were unsuccessful: the carborane units probably tend to inhibit polymerisation. However, the rates of formation of the polyoxypropylenecarboranediol are considerably higher than the rates of formation of carborane polyesters of dicarboxylic acids[32,35] (Table 3).

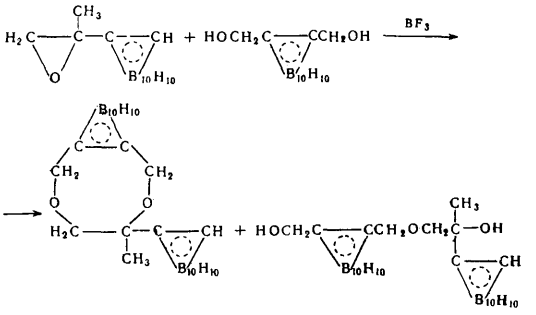
TABLE 3.

Temp., °C	Formation rate constant, mole g^{-1} min^{-1}	
	polyoxypropylenecarboranediol (Ref. 38)	poly(carborane adipate) (Ref. 33)
75	0.000344	—
120	0.00413	—
130	0.00788	—
140	0.0277	—
170	—	0.000746
190	—	0.00159
205	—	0.00248

Thermographic and thermogravimetric studies have been made to obtain information on the thermal stability of the polyoxypropylenecarboranediol. The results show that vigorous decomposition of the product begins above 250°C, and is accompanied by exothermic peaks at 330° and 435°C, probably associated with oxidising processes.

The Reviewers have made attempts to prepare a polymer by the migration polymerisation of 2'-methyloxiran-2'-ylcarborane, a product of the oxidation of isopropylcarborane with perfluoroacetic anhydride. In the presence of traces of water a resinous polymeric compound of molecular weight ~ 1000 was obtained. It proved impossible to prepare a substance of higher molecular weight. It is probable that the steric and inductive effects of the carborane nucleus are also operative here, tending to inhibit polymerisation of the 2'-methyloxiran-2'-ylcarborane.

The reaction between 2'-methyloxiran-2'-ylcarborane and bishydroxymethylcarborane is also adversely affected by the carborane system[36]. In the presence of boron trifluoride cyclic—not polymeric—compounds are formed:

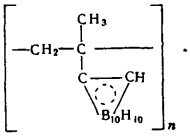


It is probable that the distance between the carborane system and the epoxy-group must be increased in order to diminish the steric effect of the carborane group. It has been remarked[31] also that attempts to polymerise 2'-methyloxiran-2'-ylcarborane have not always yielded positive results.

Carboraneurethane elastomers have been prepared by the interaction of di-isocyanates with carborane polyesters of polymethylenedicarboxylic acids[28] and also with polyoxypropylenecarboranediol[33]. The di-isocyanate is taken in slight excess over the stoichiometric quantity in order to form allophanic and biuret cross-links, which improve the mechanical properties of the elastomers. To increase the frequency of the vulcanisation network and improve the elastic properties it is proposed in certain cases[28] to introduce various polyols (glycerol, castor oil, 1,1,1-trishydroxymethylpropane, etc.) into the linear polyurethane polyester. The carboraneurethane elastomers obtained possess superior elastic properties.

Attempts have been made to obtain carborane elastomers by the polymerisation of carborane monomers, such as vinyl-, isopropenyl-, butenyl-, and allyl-carboranes. However, attempts to obtain polymers by the radical or ionic polymerisation of these compounds were unsuccessful.

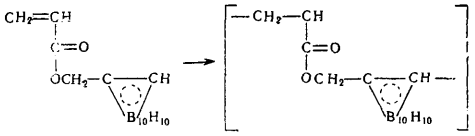
Information appeared later[37] on the polymerisation of isopropenylcarborane in the presence of 5% of aluminium chloride at 150–170°C, with the formation of a solid product of molecular weight 1790, soluble in benzene and melting above 300°C. The infrared spectra of the polymer corresponded to polyisopropenylcarborane



Trimeric isopropenylcarborane has been obtained[37] by using 50 wt.% of di-t-butyl peroxide as catalyst. With a smaller amount of the peroxide polymerisation was not observed.

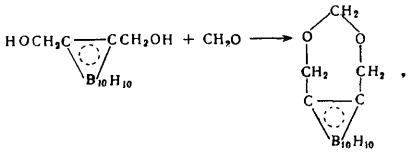
Isopropenylcarborane has been copolymerised with methyl acrylate in the presence of azoisobutyronitrile to form a polymer which softens at 45–50°C.[37] The polymerisation has been reported[38] of 1-vinylcarborane, 1-methyl-2-vinylcarborane, and 1-isopropenyl-2-methylcarborane in the presence of phenyl-lithium in ethereal solution.

Investigations have been made on the polymerisation of carboranylmethyl acrylate[27]. Radical bulk polymerisation gave a homopolymer, a brittle solid which became rubber-like at 165°C:



Copolymers of carboranylmethyl acrylate with various fluorinated acrylates have been obtained[27] by radical bulk and emulsion polymerisation.

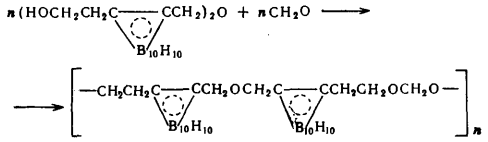
Cyclic and polymeric dialkoxymethanes have been described[27], resulting from the interaction of carboranediols with formaldehyde or with dipropoxymethane. The character of the products depends on the conditions of the reaction and the nature of the glycol used, either 1,2-bishydroxymethylcarborane or 2-carboranylpropane-1,2-diol. 1,2-Bishydroxymethylcarborane reacts with formaldehyde to yield linear polymers. Cyclic products are formed by bulk polymerisation in the presence of toluene-*p*-sulphonic acid:



Attempts to open the ring with formation of a linear dialkoxymethylene polymer were unsuccessful. The stability of the ring can be explained both by the stability of cyclic methylenedioxycarboranes and by steric hindrance to formation of a carborane polymer chain. It has been found that 1,2-substituted carboranes readily form three-membered exocyclic rings. This tendency to form cyclic structures is explained by the diminished bond length and the relatively acute external angle at which the group is attached to the carborane system.

Dimers and trimers (of molecular weight 400 and 700 respectively), or mixtures thereof, have been obtained by the interaction of 1,2-bishydroxymethylcarborane with formaldehyde in the presence of hydrochloric acid. The products were assigned a linear structure on the basis of their infrared spectra, which contained absorption bands due to terminal hydroxy-groups (2.88 μm). Other evidence of a linear structure is provided by the reaction of these products with adipoyl chloride, which results in a polymer of molecular weight 2839.

A polymer of molecular weight 4400 has been obtained by the interaction of bis-(2-hydroxyethylcarboran-1-ylmethyl) ether with formaldehyde:



The linear structure of the polymer is confirmed by the presence in the infrared spectrum of an absorption band at 2.95 μm, corresponding to terminal hydroxy-groups, and also by the interaction of the polymer with 4-methyl-1,3-phenylene di-isocyanate to give a rubberlike polymer.

However, neither cyclic nor polymeric products could be obtained from bis-(2-hydroxymethylcarboran-1-ylmethyl) ether. This fact also indicates steric hindrance by the carborane groups, inhibiting polymerisation.

Materials exhibiting high thermal stability can be obtained on the basis of carborane polymers. The production of thermostable polymers is based on a chemical bond of high energy between the atoms constituting the main polymer chain and the groups surrounding it. However, the types of bonds leading to polymers which are stable to heat are very limited. Table 4 gives the energies of rupture [sic] of a few chemical bonds.

It may be supposed that carborane polymers containing the above types of bonds as well as the carborane group will have enhanced thermal stability. Indeed, polymers containing B–O bonds together with carborane groups are stable above 400°C. Such polymers have been obtained[28] by the interaction of boric acid with 1,2-bishydroxymethylcarborane and also with 2'-methyloxiran-2'-ylcarborane. They are solids of molecular weight 1000–1200, which have softening points of 118–87°C.

Thermographic and thermogravimetric studies have been made on the thermal stability of the polymers. They show that vigorous decomposition of the product begins above 300°C. At 400°C the polymers lose about 10% of their original weight. At 800°C the losses in weight amount to 21.2%. The process is accompanied by exothermic effects over the range 490–540° and also at 725°C, probably associated with structural changes in the polymer.

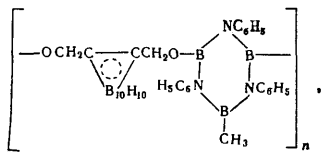
Interest has grown recently in the use of cyclic compounds of boron and nitrogen—the borazoles—for the synthesis of thermostable polymers[41]. The reason is the great thermal stability of the borazole ring, resulting from the fact that the σ-bond between boron and nitrogen atoms is supplemented by a coordinate link produced by displacement of the electron density of the lone pair of electrons from the nitrogen to the boron[42,43].

TABLE 4. Energy of rupture* of chemical bonds[39,40].

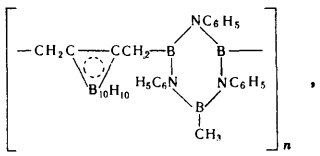
Bond	Bond energy, kcal mole^{-1}
B–O	119.3
B–N	104.3
B–C	100.0
Si–O	89.3
P–O	81.7

* Presumably the Reviewers have bond dissociation energies in mind (Ed. of Translation).

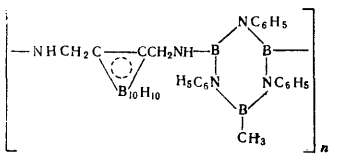
Polymers resistant to heat and to chemical reagents have been prepared from borazole and carborane compounds[44]. Polymers have been obtained from *B*-methyl-*N*-triphenylborazole together with 1,2-bishydroxymethylcarborane



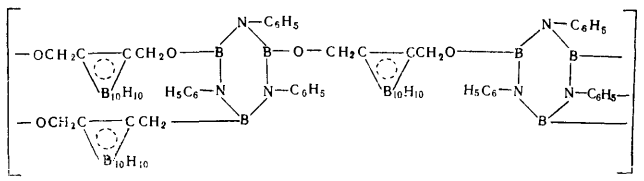
bischloromethylcarborane



or bisaminomethylcarborane



and from *N*-triphenylborazole together with 1,2-bishydroxymethylcarborane



Polymers obtained by polycondensation in the melt are brittle, transparent, pale yellow substances having molecular weights ≫ 2000. In contrast to most polyborazoles, which are readily hydrolysed in air, these polycarborane-borazoles are completely resistant to atmospheric moisture. The resistance to hydrolysis is probably influenced by steric hindrance due to the carborane groups. The structure of the polymers was assessed from their molecular weights and their infrared spectra.

Fig. 4 gives the infrared spectra of *N*-triphenylborazole *1*, bishydroxymethylcarborane *2*, and the oligomer *3* obtained from them. It is seen that the band at 1401 cm^{-1}, corresponding to the cyclic B–N bond in *N*-triphenylborazole *1* is preserved in the spectra of the oligomer *3*. The band at 2590 cm^{-1}, corresponding to the B–H bond in the carborane rings of bishydroxymethylcarborane *2* also occurs in the spectra of the oligomer. Hence it may be concluded that the oligomer consists of carborane and borazole rings.

The thermal stability of these polymers has been investigated. The heat-resistance was determined by recording thermomechanical compression curves with P = 50 g (Fig. 5). The greatest heat-resistance is shown

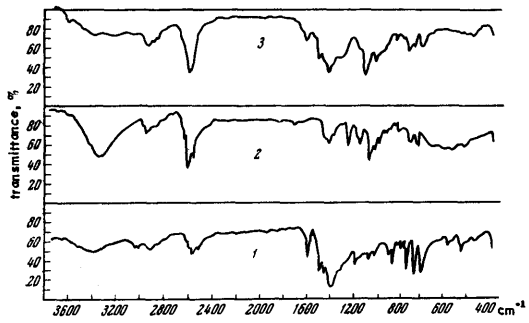


Fig.4. Infrared spectra of: 1) *N*-triphenylborazole; 2) bishydroxymethylcarborane; 3) oligomer obtained from them.

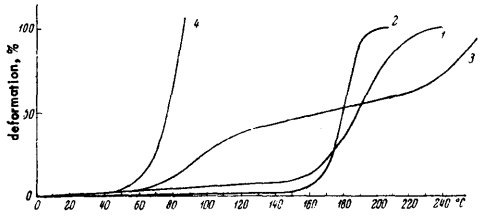


Fig.5. Thermomechanical curves of polymers based on: 1) *N*-triphenylborazole and bishydroxymethylcarborane; 2) *B*-methyl-*N*-triphenylborazole and bishydroxymethylcarborane; 3) *B*-methyl-*N*-triphenylborazole and bisaminomethylcarborane; 4) *B*-methyl-*N*-triphenylborazole and bischloromethylcarborane.

by polymers obtained from 1,2-bishydroxymethylcarborane with *N*-triphenylborazole *1* and with *B*-methyl-*N*-triphenylborazole *2*. The softening points of these polymers lie in the range 150–160°C. Those of polymers obtained from *B*-methyl-*N*-triphenylborazole with bisaminomethylcarborane *3* and with bischloromethylcarborane *4* are respectively 60° and 45°C.

The thermal stability of a polymer was determined from the change in weight of a specimen when heated in air (Fig. 6). The greatest stability is exhibited by polymers based on 1,2-bishydroxymethylcarborane with *N*-triphenylborazole *1* and with *B*-methyl-*N*-triphenylborazole *2*. When the polymers are heated in air to 400–450°C the loss in weight is ~ 1% (Fig. 6). The improved thermal stability of the polymers is possibly due to the presence of the thermostable borazole and carborane groups linked by a B–O bond, which has a high energy (Table 4). Polymers obtained from *B*-methyl-*N*-triphenylborazole with bisaminomethylcarborane *3* and with bischloromethylcarborane *4* begin to decompose vigorously above 150°C.

Phosphinocarboranes, obtained by the action of dilithium carborane on chlorophosphines containing 1–3 chlorine atoms, are highly resistant to heat and hydrolysis[45]. The product from dilithium carborane and phosphorus trichloride gives with sodium azide a compound $(B_{10}H_{10}C_2PN_2)_2$,

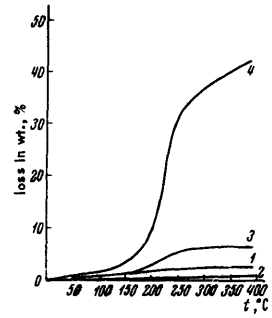
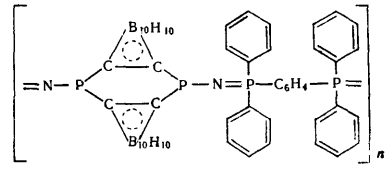


Fig.6. Thermal stability curves of borazole–carborane polymers. Numbering of curves as for Fig.5.

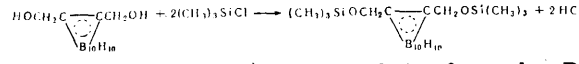
which copolymerises with $[(C_6H_5)_2P]_2C_6H_4$ to form a polymer having the structure



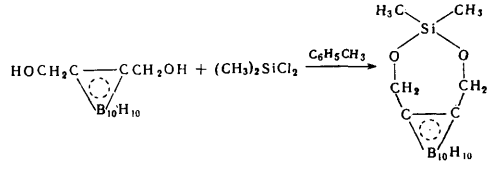
Recent investigations by the Thiokol Chemical Corporation, an American firm, show[46] that polymers highly resistant to oxidation and heat can be obtained by introducing carborane groups into a polybenzimidazole chain. Thus the sodium salt of polybenzimidazole reacts with 1-bromomethylcarborane to give the very stable polymer, polycarboranylmethylbenzimidazole. Thermogravimetric studies have shown losses of 18% and up to 25% of the original weight when the polymer is heated to 900°C in nitrogen and in air respectively.

Extremely interesting information[8,12] has been obtained on thermally stable carborane polymers containing silicon, which remain unchanged when heated to 450–500°C. Monomeric silicon-containing carboranes can be obtained[47] by the reaction of silicon chlorides with alkenylcarboranes. These reactions are catalysed by chloroplatinic acid and ferric chloride.

Reactions have been described[48] between carboranediols and methylchlorosilanes. The reaction of 1,2-bishydroxymethylcarborane with trimethylchlorosilane is represented by the equation

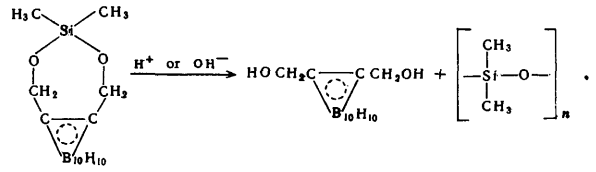


bis(trimethylsiloxymethyl)carborane being formed. Dimethyldichlorosilane reacts with the carboranediol to give a seven-membered cyclic compound



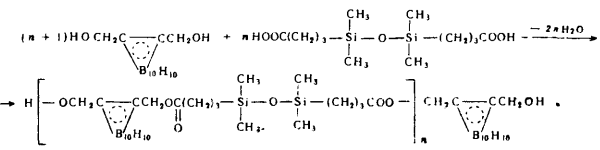
which consists of white crystals of molecular weight 260 and melting point 100°C. Attempts to open the ring to obtain a linear polymer were unsuccessful even when a catalyst was used (toluene-*p*-sulphonic acid or caustic potash),

the product being hydrolysed to the original carboranediol with formation of a polydimethylsiloxane:



An analogous compound has been synthesised[49] by the interaction of 1,2-bishydroxymethylcarborane and dimethyldichlorosilane.

The same workers[49] obtained also a series of linear carboranesiloxane polymers by the reaction between dichloropolymethylsiloxanes and 1,2-bishydroxymethylcarborane. The properties of the compounds obtained are listed in Table 5. These workers prepared carboranesiloxane oligomers by the polycondensation of bishydroxymethylcarborane with 5,5,7,7-tetramethyl-6-oxa-5,7-disilaundecane-1,11-dioic acid:



Carboranesiloxane oligomers are transparent colourless liquids of viscosity 80–90 P and molecular weight ~1000, soluble in aromatic hydrocarbons and chlorinated hydrocarbons but insoluble in alcohols and water. Thermogravimetric examination showed that the oligomers were stable up to 350°C.

Organosilicon carborane oligomers have been obtained[50] by the interaction of epoxyalkylsilanes with bishydroxymethylcarborane.

A study has been made of the migration copolymerisation of epoxypropoxypropyltriethoxysilane with bishydroxymethylcarborane. In the first stage of the process a linear polymer is formed by interaction of the epoxy-groups with the hydroxy-groups of the carborane (curves *1*, *2*, *3* at 160°, 180°, and 190°C respectively). In the second stage, when the content of epoxy-groups reaches its minimum value, the ethoxy-groups undergo alcoholysis (curves *4*, *5*, *6*, at 160°, 180°, and 190°C respectively); their content in the reaction mixture drops sharply, and the product passes from a viscous liquid to an elastic state (Fig. 7).

The resistance of the polymers to deformation on being heated was examined by determining thermomechanical curves with loads of 50 g and 100 g (Fig. 8, curves *1* and *2*). This work showed that, unlike most polymers, the product, with rise in temperature, passes into an infusible state without softening, the volume increasing at temperatures above 360°C. In view of the great thermal stability of the carboranesiloxane polymers obtained, coupled with their strong adhesion to glass and metals, and also the good dielectric properties inherent in carborane compounds, the polymers have been recommended for use as heat-insulating coatings.

There are indications that carboranesiloxane polymers having the carborane groups in side-chains possess greater thermal stability than do linear polymers having alternating carborane and siloxane units, in which the carborane groups are linked to a silicon atom directly through a methyl, methoxyl, ether, or ester group. Thus the synthesis has been described[31] of carboranesiloxane homopolymers and their copolymers with dimethylsilane having carborane groups in the side-chain, which are stable up to

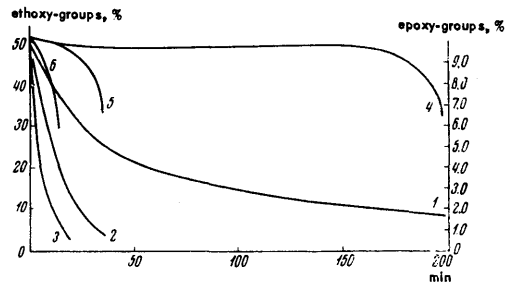
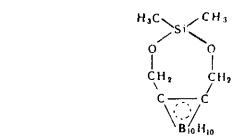
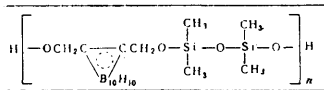
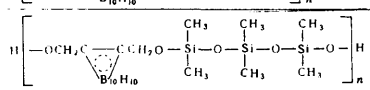
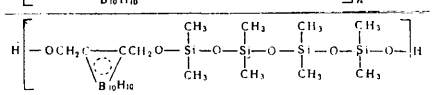


Fig. 7. Variation in quantities of epoxy-groups (1, 2, 3) and of ethoxy-groups (4, 5, 6) during reaction between epoxypropoxypropyltriethoxysilane and bishydroxymethylcarborane at temperatures of 160°, 180°, and 190°C respectively.

TABLE 5. Physicochemical properties of polydimethylsiloxymethylcarboranes.

Formula suggested for product	M	d_4^{20}	M.p., °C
	260	—	100
	580	1.5118	223.5
	900	1.4881	524
	1170	1.4726	821

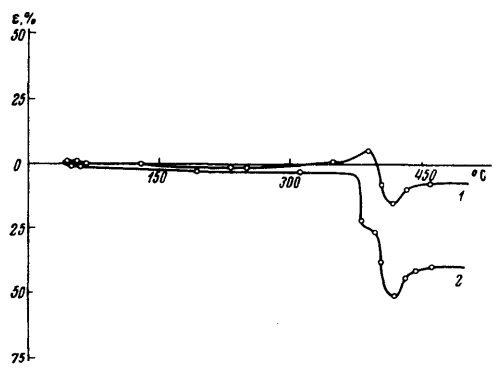
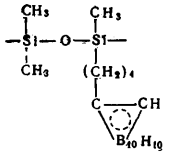


Fig. 8. Thermomechanical curves for the copolymer of epoxypropoxypropyltriethoxysilane with bishydroxymethylcarborane at loads of: 1) 50 g; 2) 100 g.

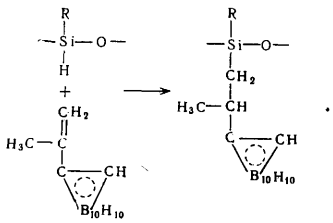
450°C. These polymers were obtained by hydrolysis and condensation reactions:†

The homopolymers have a low molecular weight owing to the formation of a large number of cyclic compounds. The copolymers are elastic solids of molecular weight ~ 13 000 and a pour point of ~ 100°C.



Thermogravimetric examination indicates that these carboranesiloxane polymers are stable up to 400–450°C in nitrogen and in air. The infrared spectra show that the carborane group remains unchanged at these temperatures. Investigation of the thermal degradation of the carboranesiloxane polymers shows that they are unaffected by heating at 350°C for 100–200 h.

Carboranesiloxane polymers have been described[51,52] with the carborane groups framing the main siloxane chain. They were obtained by the migration copolymerisation of alkenylcarboranes with polyalkylsiloxanes:



The resulting polymers are viscous or solid depending on the degree of substitution by carborane groups of hydrogen attached to the silicon atom. The solubility of the polymers in aromatic hydrocarbons and in alcohols diminishes with increase in their content of carborane groups.

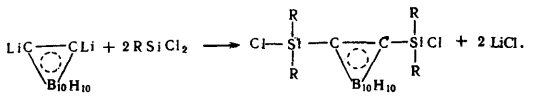
The investigations have shown that reaction between a polyalkylsiloxane and isopropenylcarborane takes place at temperatures above 200°C, hardly any reaction occurring below this temperature. However, the rates of formation of carboranesiloxane compounds are not very high even at high temperatures, as is indicated also by the formation rate constants (Table 6). The low rates of formation of carboranylsiloxanes are probably explained by steric and electronic factors due to the presence of the carborane group. Thermogravimetric analysis indicated that these polymers were stable in air up to 400–500°C.

TABLE 6. Rate constants of the formation of carborane–siloxane compounds.

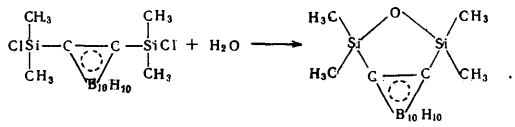
Compound	Rate constant, mmole g^{-1} min^{-1}, at		
	250°	270°	290°
Methylcarboranyloligosiloxane	$4.4 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$1.82 \cdot 10^{-4}$
Methylcarboranylcyclosiloxane	$6.25 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$1.92 \cdot 10^{-4}$

† Equations appear to have been omitted from the Russian text (Ed. of Translation).

Chlorosilyl derivatives of carborane in which the silicon atoms were directly attached to the carborane group were obtained via dilithium carborane[12]: e.g.



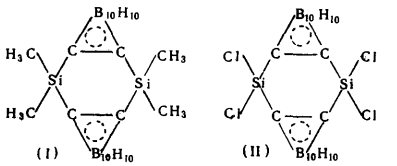
The hydrolysis of such compounds, in contrast to those described above, leads to the formation of cyclic carborane–organosilicon compounds, not the original carborane and a polysiloxane. Treatment of bischlorodimethylsilylcarborane with water yields a cyclic bisdimethylsilylcarborane:



The ammonolysis of bischlorodimethylsilylcarborane and also of bismethyldichlorosilylcarborane gave cyclic carboranedisilazanes[53]. Unlike ordinary silazanes, which react with water, the carboranesilazanes were stable to hydrolysis.

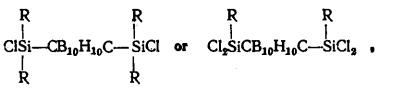
Cyclic carboranedisiloxanes and carboranedisilazanes are thermally stable up to 400°C. Above 500°C they decompose with the evolution of methane. Further rise in temperature to 600°C is accompanied by rapid decomposition with the evolution of hydrogen. Replacement by methyl groups of hydrogen attached to nitrogen improved the stability of the compounds.

Two types of thermally stable cyclic compounds

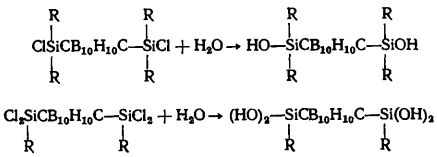


have been obtained[53]. Bisdimethylsilylenedicarborane (I) is stable to heat and hydrolysis up to 485°C. Bisdichlorosilylenedicarborane (II) does not react with water, but with ammonia the chlorine atoms are replaced by amino-groups, the carborane systems being preserved. Attempts to open the rings to give linear polymers were unsuccessful.

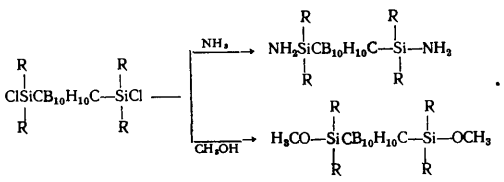
For the synthesis of thermostable carborane–organosilicon polymers, research workers turned to *m*-carborane (or neocarborane) systems, in which the positions of the carbon atoms exclude the possibility of the formation of exocyclic structures, while the stability at high temperatures is maintained. Chlorosilyl derivatives of neocarborane



were obtained via dilithium neocarborane[54]. Hydrolysis of these compounds yielded linear carborane–organosilicon compounds having terminal hydroxy-groups:

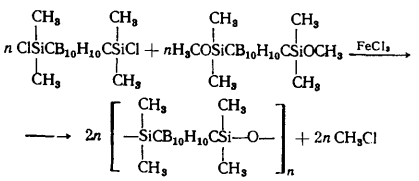


Treatment of bischlorosilylneocarboranes with ammonia and with methanol yields respectively bisaminosilyl- and bismethoxysilyl-neocarboranes:

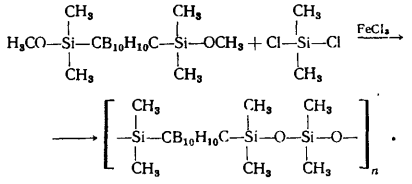


A series of silylneocarboranes have been obtained in this way [54].

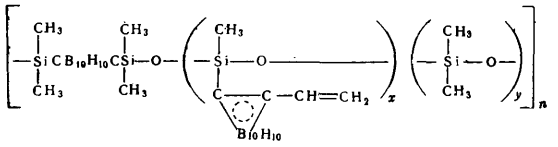
Polymers may be obtained [55] based on these compounds. The reaction of bischlorodimethylsilylneocarborane with bismethoxydimethylsilylneocarborane in the presence of iron(III) chloride at 140–190°C according to the equation



yields a polymer of molecular weight 16 000 and melting point 235–255°C, soluble in hot *N*-methylpyrrolid-2-one, decalin, chlorobenzene, and bromobenzene. Analogous polymers having different numbers of dimethylsiloxy-units have been obtained [55] by the interaction of bismethoxydimethylsilylneocarborane with dimethyldichlorosilane (or dichloropolymethylsiloxanes):



To obtain polymers by a free-radical mechanism, a few methyl groups (not more than 8%) were replaced by vinyl groups [55], especially for dichlorovinyl derivatives of carborane, yielding a polymer having the structure



The resulting polyneocarboranylenesiloxanes exhibited thermal stability above 500°C and resistance to oxidation up to 350°C. Thus, as was to be expected, these polymers were rather more thermostable than polycarboranesiloxanes with the carborane groups framing the main siloxane chain [51,52], which were stable in air up to 400–450°C.

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Summarising, we may predict that the peculiar chemical, physicochemical, and mechanical properties of polycarboranes (high thermal stability, strength, dielectric properties, adhesion to glass, metals, wood, etc.) will deservedly induce research workers to take an interest in these compounds, with the result that many new carborane polymers will be discovered which may find application in various branches of technology.

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POLYAZOLES

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I. INTRODUCTION

Modern technology has an urgent need of thermostable polymeric materials. Apart from retaining their strength at high temperatures, the polymers must meet such requirements as resistance to hydrolysis, organic solvents, and mineral acids, good dielectric properties, etc. This results from the development of such new branches of technology as rocket construction, high-speed aviation, electronics, and instrumentation, and also from the more severe demands made on polymers which are widely used in electrical and mechanical engineering, paints and varnishes, and many other branches of industry.

The demands made on the thermal stability of polymers depend on how long the polymer will be located in a high-temperature zone. For example, modern aircraft require materials which have the limiting operating temperatures indicated below[1]. Still higher demands are made on materials for spacecraft.

Length of operation, h	30 000	1000	1	5 min
Temperature, °C	177	260	540	830

During recent years broad investigations have been conducted, both abroad and in the Soviet Union, on the synthesis of heat-resistant polymers, among which the most interesting are those containing heterocycles in the main chain of the macromolecule.

Polybenzimidazoles and polypyromellitimides have already found application. It is probable that in the immediate future use will also be made of polyquinoxalines[2], polymethylquinazolones[3], polyimidazolopyrrones (pyrrones)[4,5], and polymers containing 1,3,5-triazine[6,7] and other rings.

At the present time the class of heterocyclic polymers which has been studied most thoroughly comprises the polyazoles. However, this class of polymers has not been adequately represented in the numerous reviews devoted to heat-resistant polymers[8-14]. We have tried to fill this gap, and reflect the overall progress made in synthesising polyazoles containing azole rings in the main chain and in studying their properties.

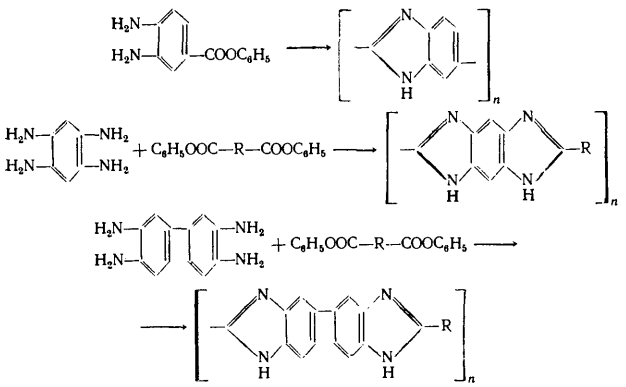
Imdividual representatives of the polyazoles—e.g. polyaminotriazoles and polythiazoles—were obtained long ago. Extraordinary interest in polyazoles as promising heat-resistant materials arose after 1959, when Brinker and Robinson, and later Marvel and his coworkers, published papers on the synthesis of polybenzimidazoles.

II. POLYBENZAZOLES

Polybenzazoles were first described by Brinker, Robinson, and Cameron [15,16], who obtained polybenzimidazoles based on biphenyl-3,3′,4,4′-tetra-amine and aliphatic dicarboxylic acids, and polybenzoxazoles based on *o*-hydroxyaminophenylalkanoic acids. The polybenzimidazoles obtained proved to be more stable than polyamides to the action of light and water. From this moment an intensive study began of the properties of polybenzazoles, in the first instance of polybenzimidazoles.

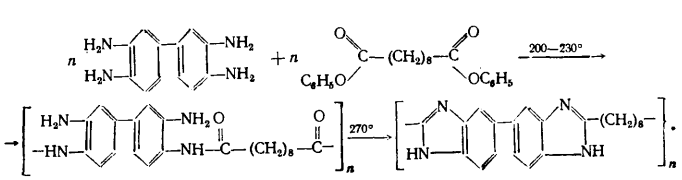
1. Methods of Preparing Polybenzazoles

Polybenzazoles have been obtained in various ways. Vogel and Marvel [17] found that aromatic polybenzimidazoles of high molecular weight can be prepared by the polycondensation of tetra-amines with diphenyl esters of dicarboxylic acids:

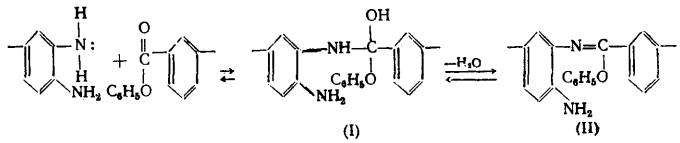


The general method developed for most of the polymers described consists in heating the reactants in the complete absence of oxygen, initially at 220–280°C, and then with the temperature raised to 400°C at 0.1 mmHg. The mass does not melt at this temperature, and the method consists essentially in solid-phase polycondensation. To obtain better results Marvel [8] proposes conducting the reaction in a rotating stainless-steel vessel, a few steel balls being placed in the mass of the polymer with the aims of stirring and improving heat transfer.

Korshak, Izyneev, and their coworkers [18-21] suggested, on the basis of elementary analysis and potentiometric titration of the reaction products, that the process in this case occurs in two stages, a polyaminoamide being formed in the first stage:

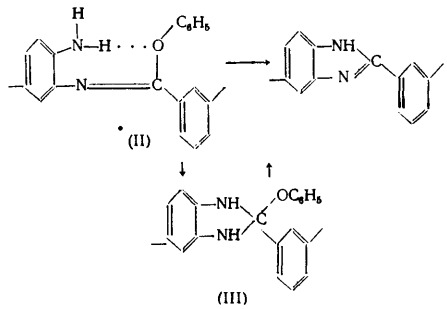


Wrasidlo and Levine [22] concluded from a detailed study of the formation of polybenzimidazoles that the reaction begins with nucleophilic attack by the amine on a carbonyl carbon atom in the diphenyl ester, an intermediate product of aldol type (I) being formed, which after dehydration gives a new intermediate product having the structure of a Schiff's base (II):



The intermediate product (II) can exhibit stereoisomerism, so that the *syn*-form can undergo intramolecular hydrogen bonding. According to these workers the formation of such hydrogen bonds promotes the intramolecular elimination of phenol and prevents the appearance of cross-linked and branched products.

The intermediate product (II) can probably exist in equilibrium with the benzimidazoline structure (III). The final process in the condensation is the elimination of phenol and formation of the polybenzimidazole:



Polybenzoxazoles of various structures have also been obtained by this process [23,24].

The overall mechanism of the formation of polybenzazoles is quite complicated. In the early stages, involving mainly the formation of polyamide units, the reaction is obviously reversible, and obeys the laws characteristic of equilibrium polycondensation. This applies in particular to the effect of excess of the reactants (Fig. 1) and to additions of monofunctional compounds. The chain termination which is usual for equilibrium polycondensation then occurs [25,26]. In the first stage, acidolysis and aminolysis of the polymer chains can obviously take place.

In the later stages, when the macromolecules contain mainly benzazole rings, the process loses its reversible character, since azole rings are exceptionally stable, as Korshak et al. [27] showed, and such polymers do not undergo degradative or exchange reactions.

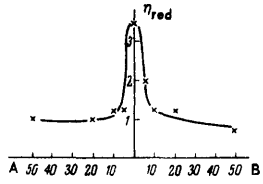
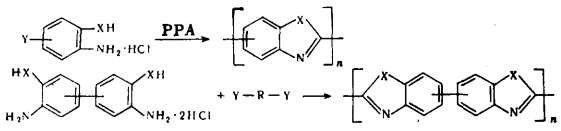
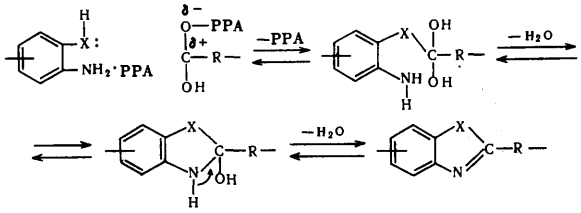


Fig. 1. Variation in reduced viscosity in formic-acid solution of poly-2,2′-octamethylene-5,5′-bibenzimidazolyl with excess (mole %) of the initial reactants:
A) biphenyl-3,3′,4,4′-tetra-amine;
B) diphenyl sebacate.

Iwakura and his coworkers[28-30] worked out a method for obtaining polybenzazoles in polyphosphoric acid (PPA). Polybenzimidazoles, polybenzoxazoles, and polybenzothiazoles of various structures were obtained according to the general scheme



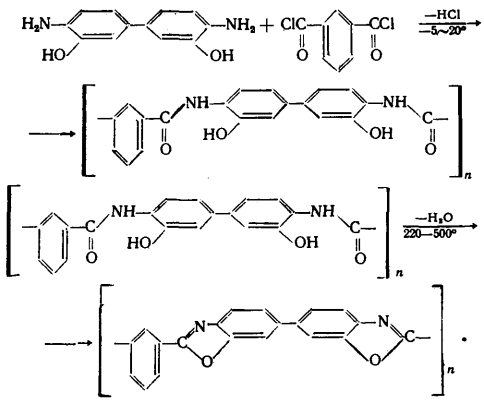
where X = NH.HCl, O, S and Y = COOH, $COOCH_3$, $CONH_2$, CN. An advantage of this method is the use of the more stable hydrochlorides instead of a tetra-amine, or an *oo'*-dihydroxy- or *oo'*-dimercapto-diamine. According to these workers[29] the benzazole polymers are formed by the reaction mechanism



where X = NH, O, S. The polyphosphoric acid enhances the reactivity of the electrophilic carbon atom in the carbonyl group, and acts as an efficient dehydrating agent.

Vogel and Marvel[17] showed that the method of interfacial polycondensation is not very suitable for the synthesis of polybenzimidazoles of high molecular weight: the polybenzimidazoles obtained had a reduced viscosity of only 0.09–0.22 dl g^{-1}.

A method which has been successfully applied to the synthesis of polybenzazoles consists in low-temperature polycondensation in a solvent followed by cyclisation of the resulting polymers at a high temperature. Kubota and Nakanishi[31], using this method, were the first to obtain completely aromatic polybenzoxazoles. In the first stage of the reaction a hydroxylated polyamide was obtained in dimethylacetamide solution, and its cyclisation yielded a polybenzoxazole:



Maksimov et al.[32] applied this method to the synthesis of polybenzothiazoles. A difficulty in this case was that the instability of the benzidinedithiol made necessary its use in the form of its hydrochloride, which was less active than the base under conditions of low-temperature polycondensation. The variation in the molecular weight during synthesis of the polymercaptopolyamide is illustrated in Fig. 2. The degree of polymerisation remains practically unchanged on cyclisation.

2. Polybenzimidazoles

Table 1 lists the properties of the polybenzimidazoles which have been described in the literature. It is seen that the properties of polybenzazoles depend fundamentally both on the structure of the original amine and on that of the acid component.

Vogel and Marvel[17] synthesised fully aromatic polybenzimidazoles from biphenyl-3,3',4,4'-tetra-amine and diphenyl esters of aromatic dicarboxylic acids. They showed that the phenyl esters gave with the tetra-amine polymers of higher molecular weight than when the acids or their methyl esters were used, since in the latter two cases polycondensation was accompanied by methylation of the amino-groups or decarboxylation as side-processes. The poly-2,2'-(*p*-phenylene)-5,5'-bibenzimidazolyl and poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazolyl which these workers obtained were highly thermostable, beginning to decompose in air only at temperatures above 500°C.

Plummer and Marvel[37] obtained polybenzimidazoles based on biphenyl-3,3',4,4'-tetra-amine and isomeric naphthalenedicarboxylic acids. The products were not so thermostable as the above polymers. These same workers showed that the condensation of diphenyl ferrocene-1,1'-dicarboxylate and of diphenyl imidazole-4,5-dicarboxylate with biphenyl-3,3',4,4'-tetra-amine yields polybenzimidazoles of fairly low reduced viscosity. The former of these polymers exhibited high thermal stability, while the latter was considerably less stable.

Dark brown or black polymers are obtained by the condensation of diphenyl fumarate or of a mixture of maleic anhydride and phenol with biphenyl-3,3',4,4'-tetra-amine. These polybenzimidazoles are to a considerable extent decomposed at 300°C.

Korshak, Izyneev, and their coworkers[18,19] obtained a poly-2,2'-octamethylene-5,5'-bibenzimidazolyl having a reduced viscosity in formic acid of 14 dl g^{-1}. Use of a vacuum of 0.01–0.001 mmHg in the second stage of the polycondensation contributed to the production of a polymer of high molecular weight and good mechanical properties.

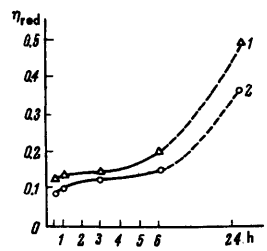


Fig. 2. Dependence of reduced viscosity of poly-3,3'-dimercaptobiphenyl-4,4'-yleneisophthalamide in H_2SO_4 on duration of reaction:
1) in the absence of pyridine; 2) in the presence of pyridine.

TABLE 1. Polybenzimidazoles.

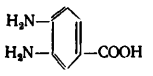
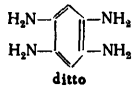
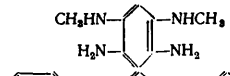
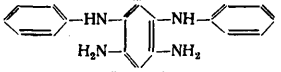
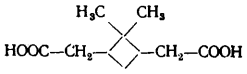
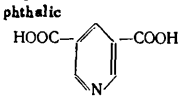
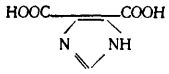
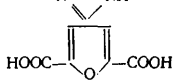
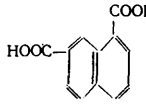
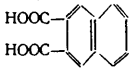
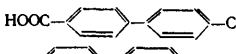
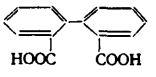
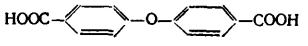
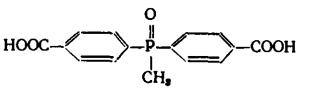
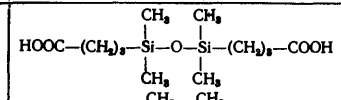
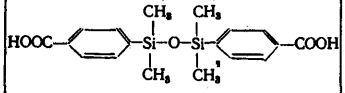
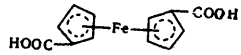
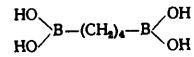
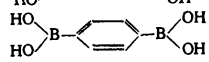
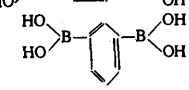
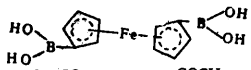
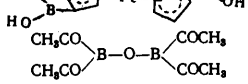
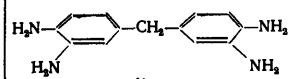
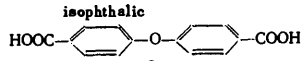
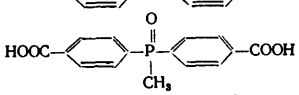
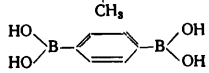
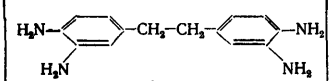
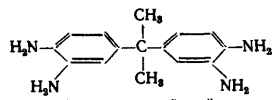
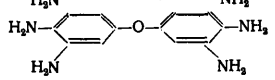
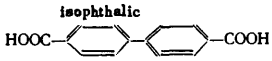
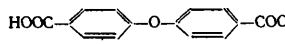
Polymer No.	Formula or name of initial components: bis-o-diamine	Formula or name of initial components: acid	Reduced viscosity in HCOOH, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	Structure*	Solubility** in: HCOOH	Solubility** in: DMF	Ref.
1	—		1.27; 1.95 (H_2SO_4)	>450	450	cr.	+	—	17, 30
2		adipic	2.51	490 decomp.	—	cr.	+	—	17
3	ditto	terephthalic	0.08 (H_2SO_4)	—	—	cr.	+	—	17
4	»	isophthalic	1.10	—	—	cr.	+	—	17
5		isophthalic	0.214 (H_2SO_4)	—	300	—			33
6		isophthalic	0.81	>500	500	—	+		34
7		oxalic	0.3 ***	—	300—400	—			35
8	ditto	malonic	0.3 ***	—	300—400	—			35
9	»	succinic	2.71	470 decomp.	300—400	—	+		34, 35
10	»	glutaric	1.19	420	300—400	—	+		34, 35
11	»	adipic	3.19	450 decomp.	300—400	am.	+	×	17, 35, 36
12	»	azelaic	0.94 (H_2SO_4)	—		am.			36
13	»	sebacic	1.4.9	470 decomp.	300—400	am.	+	+	15, 16.5, 17, 36
14	»	undecanedioic	0.73 (H_2SO_4)	—	—	am.			36
15	»	$HOOC-(CH_2)_{20}-COOH$	—	—	—	—	—		36
16	»	$HOOC-CH=CH-COOH$	0.07 (DMS)	250 decomp.	200	—	+		37
17	»		1.38	400 decomp.	—	—	+		17
18	»	terephthalic	1.00	—	500	cr.	+	—	17, 28
19	»	isophthalic	3.34	—	500	am.	+	×	17, 28
20	»	phthalic	5.01	—	500	—	+		34
21	»		1.48	—	—	cr.	+	×	17
22	»		0.16	550 decomp.	550	—	+		37
23	»		0.74	480 decomp.	—	cr.	+	+	17
24	»		2.70	—	—	am.	+	—	17
25	»		1.26 (H_2SO_4)	>550 decomp.	500—550	—	—	—	37
26	»		1.10	550 decomp.	350—450	—	+		37
27			0.61	400 decomp.	150—350	—			37
28	ditto		0.86 (H_2SO_4)	—	—	cr.	×	—	17
29	»		2.99	430	300—350	am.	+	+	17
30	»		1.14	460—470	—	cr.	+	×	38, 39
31	»		—	520	—	—	+	×	40

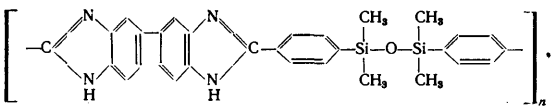
TABLE 1 (cont'd).

Polymer No.	Formula or name of initial components: bis-o-diamine	Formula or name of initial components: acid	Reduced viscosity in HCOOH, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	* Structure	Solubility** in: HCOOH	Solubility** in: DMF	Ref.
32	»		0.12 (C_2H_5OH)	215	—	am.	+	+	41
33	»		0.49 (DMS)	420—450	—	—	+	+	41
34	»		0.20	—	150—250	—			37
35	»	HOOC—$(CF_2)_3$—COOH	0.20 (DMS)	300 decomp.	220—230 (in argon)	—	+		37
36	»	HOOC—$(CF_2)_4$—COOH	—	—	240	—			40
37	»	HOOC—$(CF_2)_6$—COOH	0.17 (H_2SO_4)	300 decomp.	250	—	+		37
38	»		—	350—370	—	—	+		42
39	»		0.35 (DMS)	—	500—600	cr.			42, 43
40	»		0.15 (DMS)	>550	450—500	—		+	43
41	»		0.14 (DMA)	—	350—550	—		+	43
42	»		0.26***	does not melt	400—500	—			44
43		adipic	8.16	290—300; 200 glass point	460	lcr.	+	+	45
44	ditto	sebacic	4.62	260—270; 200 glass point	460	am.	+	—	45
45	»	terephthalic	1.06	400—410	500	am.	+	—	45
46	»	isophthalic	1.82	380—390	490	am.	+	—	45
47	»		1.58	350—370	500	am.	+	+	38
48	»		1.00	380—400	490	am.	+	+	38
49	»		0.16	500	500	cr.	+	+	38
50		malonic	0.63 (*m*-cresol)	—	—	am.			15
51	ditto	adipic	—	—	—	—			15
52		adipic	—	—	—	—			
53		sebacic	2.5	240—245	300—350	—	+	+	46
54	ditto	isophthalic	1.26	390	500	—	+	+	39, 46
55	»		0.7 (DMS)	—	—	—	+		39
56	»		0.5 (DMS)	—	—	—	+		39

* Abbreviations: cr. = crystalline; lcr. = low degree of crystallinity; am. = amorphous polymer.
** Symbols: + = soluble; × = partly soluble; − = insoluble; DMF = dimethylformamide.
*** Intrinsic viscosity.
**** DMA = dimethylacetamide; DMS = dimethyl sulphoxide.

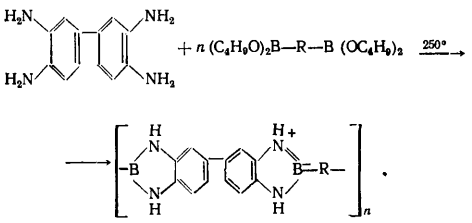
Plummer and Marvel[37] synthesised polybenzimidazoles based on biphenyl-3,3',4,4'-tetra-amine and perfluoropolymethylenedicarboxylic acids, in the hope that they would be more thermostable than polymers based on ordinary aliphatic acids. However, the fluorinated polybenzimidazoles already begin to decompose at 200–250°C. Other workers[47,48] have also referred to the low thermal stability of polyperfluoromethylenebenzimidazoles.

Mulvaney and Marvel[41] described the properties of a polybenzimidazole having the structure

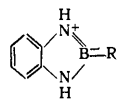


This polymer is less thermostable, possesses a higher solubility, and melts at a far lower temperature than aromatic polybenzimidazoles. The polymer begins to melt at 420–450°C, but even after being heated to 450°C it retains its solubility in dimethyl sulphoxide, dimethylformamide, and formic acid.

Mulvaney, Bloomfield, and Marvel[43], as well as Bamford and Fordham[42], obtained polybenzoborimidazolines from biphenyl-3,3′,4,4′-tetra-amine and the appropriate diboronic esters:



A cyclic molecule containing a boron atom

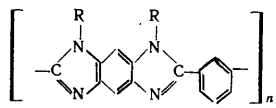


possesses a system of π-electrons, and its ultraviolet spectrum is similar to that of benzimidazole[49-51]. In view of their aromatic character these polymers are quite thermostable, the loss in weight in nitrogen at 450–500°C being ~10% for the polymer based on benzene-*p*-diboronic acid.

Polybenzazoles containing respectively oxygen and phosphorus in the main chain have been prepared and investigated. Polybenzimidazoles containing these elements have been described by Frunze et al.[38] and also by Foster and Marvel[39]. The introduction of oxygen improves the solubility and should probably improve the mechanical characteristics of polybenzazoles. Thus from biphenyl-3,3′,4,4′-tetra-amine and diphenyl oxy-*pp*′-dibenzoate a polymer has been obtained possessing a crystalline structure and soluble in sulphuric acid, formic acid, and dimethyl sulphoxide in the cold, and in dimethylformamide and tricresol on heating. The polymer obtained from diphenylmethane-3,3′,4,4′-tetra-amine and the same ester is soluble in dimethylformamide in the cold. A polybenzimidazole containing phosphorus, which has the interesting and important property of non-flammability, has been obtained by the interaction of diphenylmethanetetra-amine and diphenyl methyloxodiphenylphosphorane-*pp*′-dicarboxylate. When the polymer is introduced into the burner flame, it slowly smoulders and chars, but on withdrawal from the flame it is immediately extinguished. The self-quenching of this polymer is due to the presence of the phosphoryl group (phosphorus content 6.8%). An analogous phenomenon has been observed with phosphorus-containing polyamides[52].

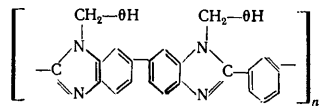
In all the preceding cases the properties—mainly the solubility—of the polybenzimidazoles were varied by a suitable choice of acid components having various structures. However, it is evident from the data which are cited that a considerable improvement in solubility was accompanied by a sharp fall in thermal stability. More recent work has shown that the properties of polybenzimidazoles can be modified, while adequate thermal stability is maintained, also by varying the structure of the initial amine, e.g. by introducing various substituents into the molecule of a fully aromatic tetra-amine, or by obtaining mixed polymers.

Marvel and his coworkers[33,34] prepared *N*-substituted polybenzimidazoles of general formula



where R = C_6H_5, CH_3. The phenylated polymer showed practically the same thermal stability as the analogous unsubstituted polybenzimidazole. The methylated polymer began to decompose in air at 300°C.

An *N*-substituted polybenzimidazole has recently been synthesised[53] having the structure

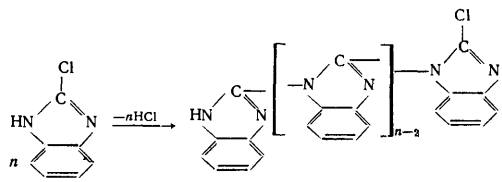


where θ represents



by reaction between the sodium salt of polybenzimidazole and 1-bromomethylcarborane. Polycarboranylmethylbenzimidazole loses only 25% of its weight when heated in air to 900°C.

By heating 2-chlorobenzimidazole at its melting point, Harrison and Ralph[54] obtained an insoluble high-melting polymer, which did not decompose up to 400°C:



Frunze et al.[45] have synthesised several polybenzimidazoles based on diphenylmethanetetra-amine and dicarboxylic acids. These polymers are yellow to brownish vitreous products, which soften between 260° and 400°C and possess a mainly amorphous structure. The ultraviolet spectra of these polybenzimidazoles[55] have absorption maxima close to those of model compounds, but exhibit some bathochromic and hypsochromic shifts, which were referred to also by Vogel and Marvel[17] when discussing fully aromatic polybenzimidazoles. The polybenzimidazoles based on diphenylmethanetetra-amine possess somewhat better solubility than the corresponding polymers based on benzidinediamine, while having approximately the same thermal stability.

Polybenzimidazoles have been described based on a tetra-amine containing an ether link between phenyl groups[39,46]. Korshak et al.[56] suggested preparing polybenzazoles containing various substituents on the central carbon atom of

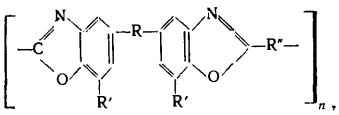
the initial amine. The resulting polymers were distinguished by better solubility.

Mixed polybenzimidazoles containing residues of two different dicarboxylic acids have been synthesised by Korshak and his coworkers[40,57]. The thermal stability of the mixed polybenzimidazoles is somewhat below that of the homopolymers, as is evident from Fig. 3, which shows the variation in the decomposition temperature with the composition of the initial mixture. Mixed polybenzimidazoles containing units of an aliphatic dicarboxylic acid decompose at lower temperatures (in the range 400–520°C) than do polybenzimidazoles synthesised solely from aromatic components. Thus the decomposition point of polybenzimidazoles obtained from biphenyl-3,3′,4,4′-tetra-amine and diphenyl isophthalate and terephthalate lies in the range 460–520°C.

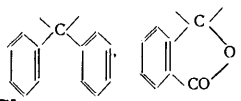
3. Polybenzoxazoles and Polybenzothiazoles

Great interest has recently been evinced in polybenzoxazoles and polybenzothiazoles (Table 2), analogues of polybenzimidazoles, since it has been supposed that they will show greater resistance than polybenzimidazoles to oxidative thermal degradation.

Several communications appeared almost simultaneously on the synthesis of polybenzoxazoles based on 4,4′-diaminobiphenyl-3,3′-diol[23,31,58]. It was noted that polybenzoxazoles are inferior to polybenzimidazoles in solubility. In order to improve the solubility of the former, Korshak et al.[24,60,61] synthesised polymers containing various substituents in the benzene ring of the benzoxazole, of general formula



where R = $C(CH_3)_2$, $C(CH_3)(C_6H_5)$, $C(C_6H_5)_2$,



and R′ = H, CH_3, Cl.

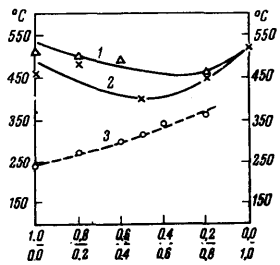


Fig. 3. Variation, with molar composition of mixed polybenzimidazoles based on biphenyl-3,3′,4,4′-tetra-amine, in:
1) decomposition temperature of polymers from sebacic and isophthalic acids;
2) decomposition temperature of polymers from terephthalic and isophthalic acids;
3) softening point of polymers from sebacic and isophthalic acids.

The resulting polymers, while possessing high thermal stability (loss in weight begins at 400–500°C when R″ represents an aromatic group), dissolve in a wide range of organic solvents—chloroform, tetrachloroethane, tricresol, benzyl alcohol, pyridine, dimethylformamide, etc.—except in the case of polymers containing halogen in the side-chain and with the central carbon atom forming part of a phthalidylidene group. Polymers in which R″ represents an aromatic radical pass into an infusible and insoluble state when heated to 450°C. Unfortunately, the authors do not discuss the effect of molecular weight on the solubility of the polybenzoxazoles obtained.

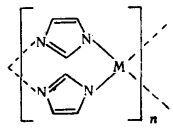
Polybenzothiazoles were first synthesised in 1962 by Kipriyanov and Mushkalo[63]. However, these workers merely obtained an oligomeric condensation product of 4-amino-3-mercaptobenzoic acid. Hergenrother et al.[62] suggested that polybenzothiazoles should be synthesised in two stages: in the first stage a precondensate of low molecular weight is formed in boiling diethylaniline solution, and this passes on further condensation in the solid phase into a polybenzothiazole of high molecular weight. Imai et al.[29,30] synthesised several new polybenzothiazoles and isomeric polybenzoxazoles by their method of polycondensation in polyphosphoric acid.

All the authors note the great stability to heat and thermal oxidation of the polybenzothiazoles, which, however, are soluble only in concentrated sulphuric acid.

III. POLYIMIDAZOLES

In the case of polyazoles not containing fused rings—in contrast to polybenzazoles, where until recently attention has been paid mainly to benzimidazole derivatives—most of the work has been done on the synthesis of polythiazoles, the first information on which appeared during the Second World War. Few papers have been concerned with the synthesis of polyimidazoles, and we have found none on that of polyoxazoles.

Brown and Aftergut[64] prepared polyimidazoles of general formula



where M is a bivalent metal. The products were insoluble in organic solvents, infusible, and quite thermostable, showing no loss in weight when heated in nitrogen to 500–575°C.

A polymer possessing semiconductor properties was obtained by the pyrolysis of 2,4,5-tri-iodoimidazole and 1,2,4,5-tetraiodoimidazole[65].

IV. POLYTHIAZOLES

Erlenmeyer and his coworkers[66,67] were the first to obtain polythiazoles, but they did not examine the properties of the products. Mulvaney and Marvel[68], and somewhat earlier some Japanese investigators[69], continued Erlenmeyer's work on the synthesis of polythiazoles. Several papers have appeared recently reporting detailed investigations of the properties of polymers of this type, information on which is given in Table 3.

TABLE 2. Polybenzoxazoles and polybenzothiazoles.

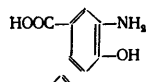
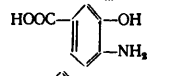
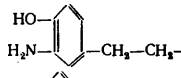
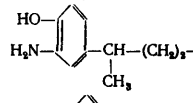
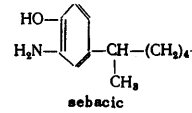
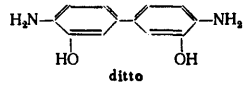
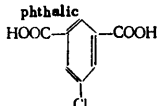
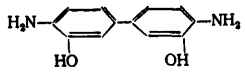
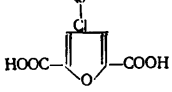
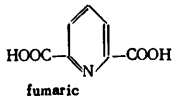
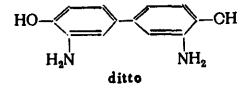
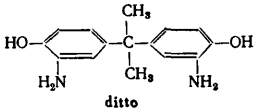
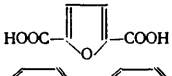
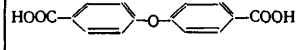
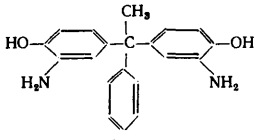
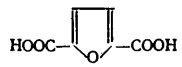
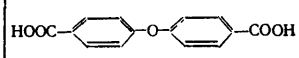
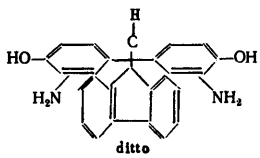
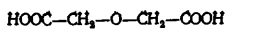
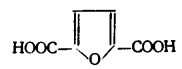
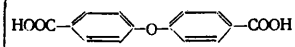
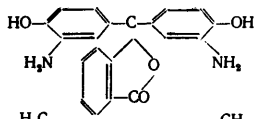
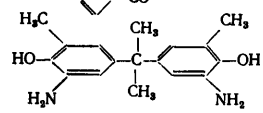
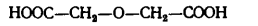
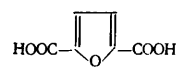
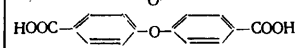
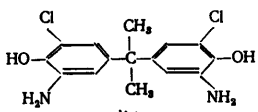
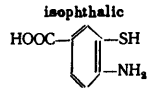
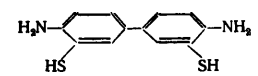
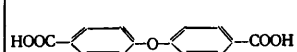
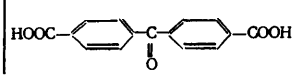
Polymer No.	Formula or name of initial components: bis-o-aminophenol or bis-o-aminothiol	Formula or name of initial components: acid	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	Structure*	Solubility** in: HCOOH	Solubility** in: DMF	Solubility** in: other organic solvents	Ref.
1	—		2.21	—	450	am.	—	—		30
2	—		1.40	—	500	cr.	—	—		30
3	—		0.4—1.5 (*m*-cresol)***	—	—	—				16
4	—		—	—	—	—				16
5	—		—	—	—	—				16
6		sebacic	0.40	250° (softens slightly)	300°	—	+	am.	*m*-cresol	16, 29
7	ditto	terephthalic	1.36	—	500—550	am.	—	—		29
8	»	isophthalic	1.50	—	500	am.	—	—		29
9	»	phthalic	0.93	—	—	—	—			23
10	»		0.20	—	—	—			H_2SO_4 (75%)	23
11			—	—	—	—				59
12	ditto		—	—	—	—				59
13	»	fumaric	—	—	—	—				59
14		sebacic	1.34	250° (softens slightly)	300	am.				29
15	ditto	terephthalic	1.60	—	—	am.	—	—		29
16	»	isophthalic	2.09	—	450—500	am.	—	—		29
17		adipic	0.32	—	420	am.	×	+	chloroform, THF***, pyridine	60, 61
18	ditto	sebacic	0.38	—	420	am.	—	+	ditto	24
19	»	$HOOC-CH_2-O-CH_2-COOH$	0.18	—	250	am.	×	×		60, 61
20	»	terephthalic	0.16	—	510	lcr.	+	+	chloroform	60, 61
21	»	isophthalic	0.15	—	500	am.	+	+	chloroform, THF, pyridine	60, 61
22	»		0.12	—	450	am.	—	+	ditto	60, 61
23	»		0.21	—	420	am.	—	—	»	60, 61
24		adipic	0.26 (cresol)	—	350	am.	×	+	chloroform, THF, pyridine	60, 61
25	ditto	sebacic	0.3 (cresol)	—	350	—	+	+	ditto	60, 61
26	»	$HOOC-CH_2-O-CH_2-COOH$	0.22 (cresol)	—	200	—	—	+		60, 61
27	»	terephthalic	0.12 (cresol)	—	300	—	—	—	»	60, 61
28	»	isophthalic	0.15 (cresol)	—	320	—	—	+	»	60, 61

TABLE 2 (cont'd).

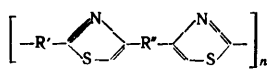
Polymer No.	Formula or name of initial components: bis-o-aminophenol or bis-o-aminothiol	Formula or name of initial components: acid	Reduced viscosity in H_2SO_4 at 20°C, dl/g	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in air	* Structure	Solubility** in: HCOOH	Solubility** in: DMF	Solubility** in: other organic solvents	Ref.
29	〃 〃		0.11 (cresol)	—	320	—	—	+	〃 〃	60, 61
30	〃 〃		0.12 (cresol)	—	350	—	—	+	〃 〃	60, 61
31		adipic	0.28 (cresol)	—	400	am.	—	—	chloroform, THF	60, 61
32	ditto	sebacic	0.27 (cresol)	—	400	lcr.	—	×	chloroform, THF, pyridine	60, 61
33	〃		0.25 (cresol)	—	300	am.	—	—		60, 61
34	〃	terephthalic	0.15 (cresol)	—	400	am.	—	×	chloroform, THF, pyridine	60, 61
35	〃	isophthalic	0.18 (cresol)	—	400	am.	—	×	ditto	60, 61
36	〃		0.15 (cresol)	—	300	am.	—	+	〃	60, 61
37	〃 〃		0.15 (cresol)	—	350	am.	—	×	〃	60, 61
38		sebacic	0.17	—	330	am.	—	—		24
39		adipic	0.32	—	400	lcr.	+	+	chloroform, THF, pyridine	60, 61
40	ditto	sebacic	0.34	—	300	lcr.	+	+	ditto	60, 61
41	〃		—	—	200	am.	×	×		60, 61
42	〃	terephthalic	0.17 ($CHCl_3$)	—	400	am.	—	×	〃	60, 61
43	〃	isophthalic	0.18 ($CHCl_3$)	—	400	am.	—	×	〃	60, 61
44	〃		0.15 ($CHCl_3$)	—	300	am.	—	+	〃	60, 61
45	〃		0.2 ($CHCl_3$)	—	300	am.	—	+	〃	60, 61
46		sebacic	—	—	220	lcr.	—	—		60, 61
47	ditto	isophthalic	—	—	180	am.	—	—		60, 61
48	〃		2.03 (H_2SO_4)	>450	500	am.				30
49		sebacic	0.31 (H_2SO_4)	—	300	cr.	+		cresol	29
50	ditto	terephthalic	1.02 (H_2SO_4)	—	550	am.	—	—		29, 62
51	〃	isophthalic	0.43 (H_2SO_4)	466,527, 910(glass point)	600	am.	—	—		29, 62
52	〃		0.62 (H_2SO_4)	288 (glass point)	—	—				62
53	〃		0.36 (H_2SO_4)	—	—	—				62

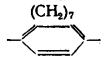
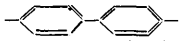
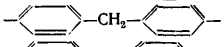
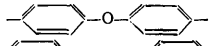
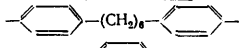
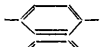
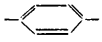
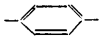
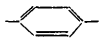
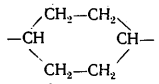
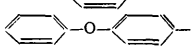
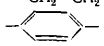
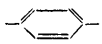
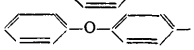
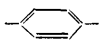
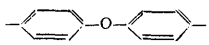
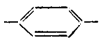
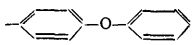
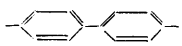
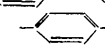
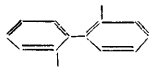
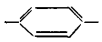
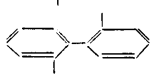
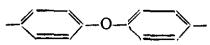
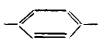
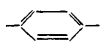
* Abbreviations: cr. = crystalline; lcr. = low degree of crystallinity; am. = amorphous polymer.

** Symbols: + = soluble; × = partly soluble; – = insoluble; DMF = dimethylformamide.

*** Intrinsic viscosity.

**** THF = tetrahydrofuran.

TABLE 3. Polythiazoles of general formula 

Polymer No.	R′	R″	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C: melting or softening	Temperature, °C: start of decomp. in N_2	Ref.
1	—	—	—	—	—	66
2	—	$(CH_2)_4$	—	—	—	66
3	—	$(CH_2)_7$	—	—	—	66
4	—		0.23	>520	500—700	70, 71
5	—		0.24	>520	400 (20%)	80
6	—		0.47	>520	400 (20%)	70
7	—		0.38	>520	525 (40%)	70
8	—		0.40	440—448		70
9	CH_2		0.24	500	500 *	71
10	$(CH_2)_2$		0.87 (HCOOH)	164—265	290 *	71
11	$(CH_2)_4$	—	—	—	—	66
12	ditto	$(CH_2)_4$	—	—	—	66
13	»	$(CH_2)_7$	—	—	—	66
14	»		3.96 (HCOOH)	164—265	487—490 *	67, 68, 71
15	$(CH_2)_7$	—	—	—	—	66
16	ditto	$(CH_2)_4$	—	—	—	66
17	»	$(CH_2)_7$	—	—	—	66
18	$(CH_2)_8$		1.78 (HCOOH)	164—265	487—490 *	71
19			1.00	226	440 (20%)	72
20			0.30	>500	500 *	67, 68, 71
21	ditto		0.22	>500	500 *	71, 72
22			0.17	>500	500 *	68, 71
23	ditto		0.49	340	450 (20%)	71, 72
24			0.13	>500	500 *	71
25	ditto		0.33	>500	500 *	71
26			0.19	>500	500 *	71
27			0.52	164—265	500 *	71
28			0.59 (HCOOH)	164—265	500 *	71
29	$(CH_2)_4$; 		0.34	240		71

* In air.

Longone and Un[70] obtained polybenzothiazoles from a dithioamide and aromatic and mixed aliphatic and aromatic bis-α-bromoketones. All the polymers obtained were insoluble in organic solvents, including dimethyl sulphoxide, dimethylacetamide, and formic acid, but readily dissolved in concentrated sulphuric acid, and were infusible highly crystalline substances of high molecular weight. These polymers possess excellent thermal stability, but probably will not find wide practical application owing to difficulties arising in processing and their poor mechanical characteristics.

The most thorough study has been made by Sheehan el at.[71] They prepared a series of polythiazoles by the reaction

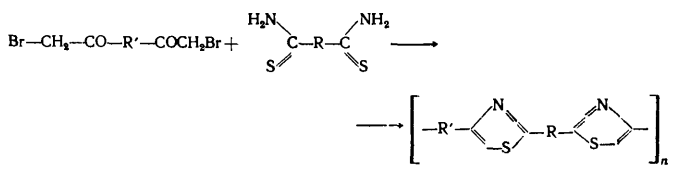


TABLE 4. Polypyrazoles.

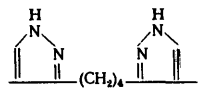
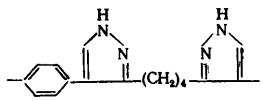
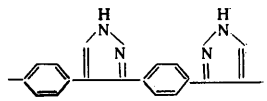
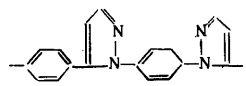
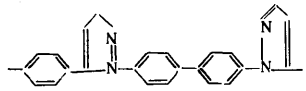
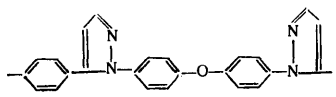
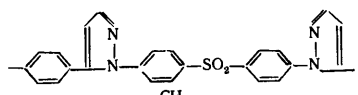
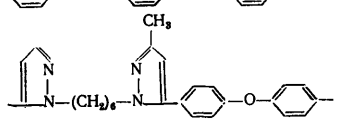
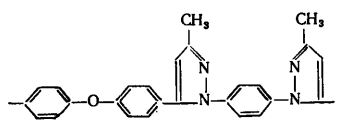
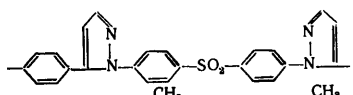
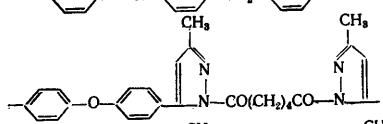
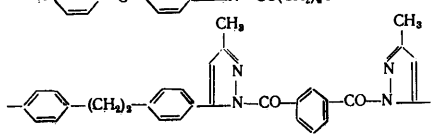
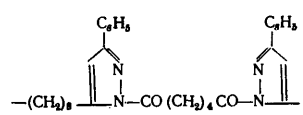
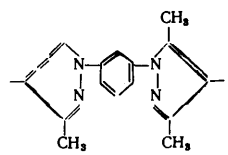
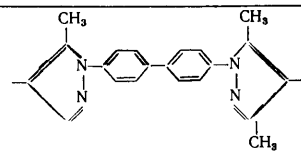
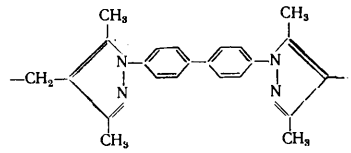
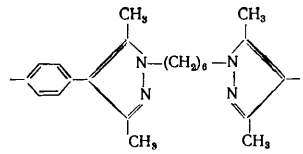
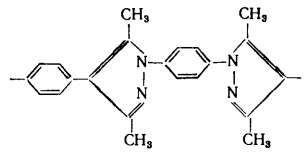
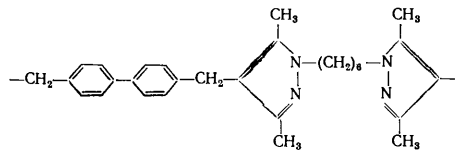
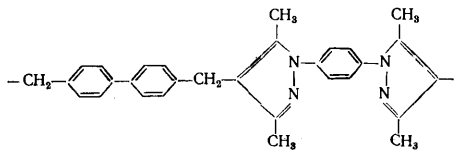
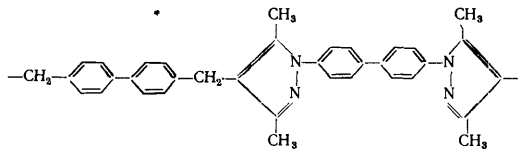
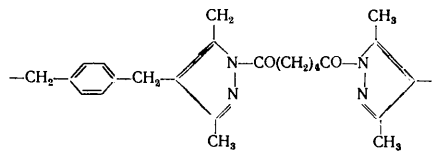
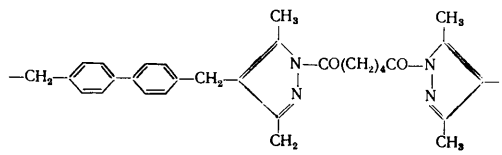
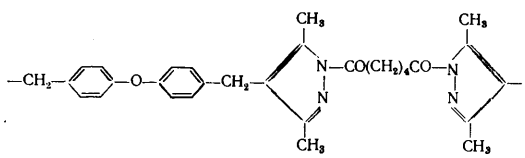
Polymer No.	Structural unit	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C		Ref.
			melting	start of decomp. in air	
1		0.2	350—374	—	78
2		0.3	440	—	78
3		0.24	>500	—	78
4		0.13 (HCOOH)	—	600 (20%)	77
5		—	—	—	77
6		—	—	—	77
7		—	—	—	77
8		0.12	118—124	—	78
9		0.09	122—140	—	78
10		0.14	218—225	—	74
11		0.10	210—220	—	74
12		0.12	260—280	—	74
13		0.08	100—120	—	74
14		1.5—2.0 (HCOOH)		450 (in nitrogen)	76

TABLE 4 (cont'd).

Polymer No.	Structural unit	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C: melting	Temperature, °C: start of decomp. in air	Ref.
15		0.54; 0.70 (H_2SO_4)	—	500	80
16		—	—	350	80
17		0.25	156—174	—	79
18		0.15	262—265	—	79
19		0.08	141—146	—	79
20		0.09	120—132	—	79
21		0.19	180—190	—	80
22		0.12	230—300	—	81
23		0.1	228—230	—	81
24		0.15	245—256	—	81

and concluded that only those polymers which had low heat-resistance possessed satisfactory mechanical properties. Other workers hold the same view[72].

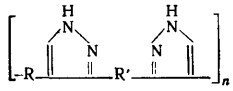
An interesting result of the work of Sheehan et al. is the preparation of polythiazoles based on *oo'*-bisbromoacetylbiphenyl, possessing satisfactory mechanical properties and high thermal stability (up to 500°C). They also obtained[73] a fibre-forming polythiazole.

The introduction of side-chains—methyl and carboxyl substituents—into the thiazole ring produces no appreciable improvement in the properties of the polythiazoles[71].

V. POLYPYRAZOLES

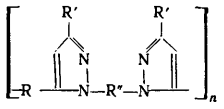
In 1963 Korshak et al.[74] described for the first time the preparation of polypyrazoles by the reaction of bis-β-diketones with dihydrazides of dicarboxylic acids. A later paper by Korshak et al.[75] has further elaborated methods for the synthesis of polypyrazoles. American workers have also published papers on the synthesis of polypyrazoles[76,77]. According to their structure these polymers can be divided into three main types.

Polypyrazoles of general formula



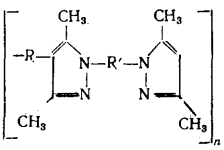
have been obtained by the method of Korshak et al.[78] from bisdiazo-compounds and *p*-diethynylbenzene or butadiyne. They were high-melting products of molecular weight around 10 000, soluble in dimethylformamide and cresol. Unfortunately, the authors gave no indication of the thermal stability of these polymers.

Polypyrazoles of general formula



have been obtained by the interaction of bis-β-diketones of the type $R'COCH_2CORCOCH_2COR'$ with various dihydrazines or dihydrazides[74,77,79-81]. In this case the reaction goes in two stages, involving the initial formation of a polyhydrazone, which then cyclises to produce the polypyrazole. The first stage can be conducted in a solvent[77,79]. With dihydrazides of dicarboxylic acids[74] polypyrazoles are obtained which can be regarded formally as *N*-substituted polyamides.

A third group of polypyrazoles corresponds to the general formula

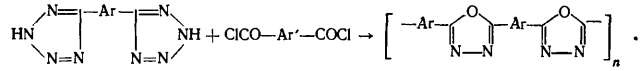


The heat-resistance of polymers of this type is lower than that of polypyrazoles containing no alkyl substituents, but their thermal stability must be expected to be higher owing to the absence of a mobile hydrogen atom in the pyrazole ring.

VI. POLYOXADIAZOLES

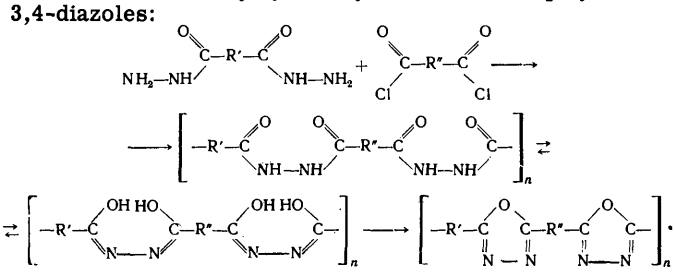
Most of the work on the synthesis of polyoxadiazoles has been done on the preparation of polyoxa-3,4-diazoles. Fully aromatic polyoxa-3,4-diazoles possess not only excellent resistance to heat, chemicals, and light but also good mechanical properties, which enables films and fibres to be made from them. Table 5 gives some properties of polyoxa-3,4-diazoles obtained by various methods.

Abshire and Marvel[86], elaborating the method of Sauer et al.,[87] prepared polyoxa-3,4-diazoles from bistetrazoles and chlorides of dicarboxylic acids by the reaction



However, the molecular weights of polymers obtained by this method were not very high.

Frazer and Wallenberger[85,88,89] proposed a two-stage method for the synthesis of polyoxadiazoles. Under conditions of low-temperature polycondensation in the first stage macromolecular polyhydrazides are obtained, which are then converted by cyclodehydration into the polyoxa-3,4-diazoles:



Films and fibres can be obtained from the melt only with those polyoxadiazoles which fuse below 350°C. Aromatic polyoxadiazoles which melt above this temperature are processed at the polyhydrazide stage, and cyclisation is accomplished in the finished goods.

A two-stage synthesis of polyoxa-3,4-diazoles has been used also by Korshak et al.[84,90,91], who obtained a polyoxadiazole containing ether links which was a promising material for the manufacture of a heat-resistant fibre.

It has also been proposed to obtain polyoxa-3,4-diazoles in the melt, starting from the corresponding polyhydrazides[82]. However, this method is restricted to a narrow range of aliphatic polyoxadiazoles.

Iwakura et al.[83] synthesised polyphenyleneoxa-3,4-diazoles in polyphosphoric acid or oleum solution, the latter solvent giving polymers of higher molecular weight. Soviet workers have also reported[92] the preparation of polyoxa-3,4-diazoles in oleum.

A paper has appeared recently[93] on the synthesis of polyoxa-2,4-diazoles by the series of reactions

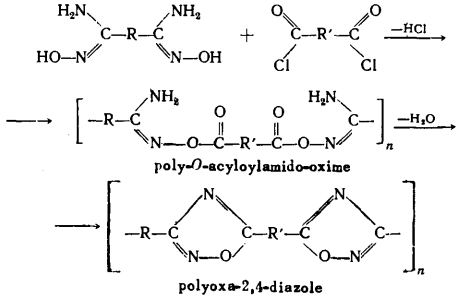
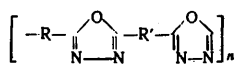
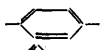
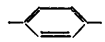
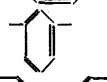
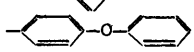
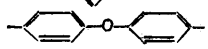
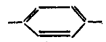
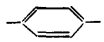
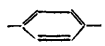
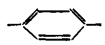
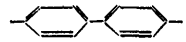
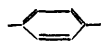
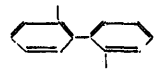
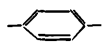
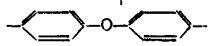
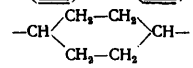
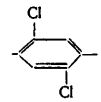
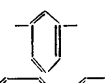
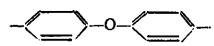
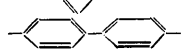
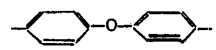


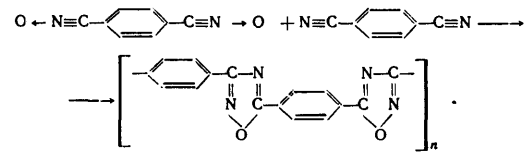
TABLE 5. Oxa-3,4-diazoles of general formula 

Polymer No.	R	R′	Reduced viscosity in H_2SO_4, dl g^{-1}	Temperature, °C		Ref.
				melting or softening	start of decomp. in air	
1	$(CH_2)_8$	$(CH_2)_8$	0.45 * (cresol)	90—110	300	82
2	$(CH_2)_9$	$(CH_2)_9$	0.40 * (cresol)	66—82	300	82
3	$(CH_2)_{10}$	$(CH_2)_{10}$	0.41 * (cresol)	64—100	300	82
4			3.7	—	450	83
5			2.2	—	450	83
6			0.95	370	430	84
7	—		0.60	—	—	85
8	—		0.1	—	—	85
9	$(CH_2)_4$	$(CH_2)_7$	0.3	—	—	85
10	$(CH_2)_4$		0.50	—	—	85
11	$(CH_2)_7$		0.15	—	—	86
12	$(CH_2)_8$		0.4	—	—	85
13			0.5	—	450	85
14			0.10	—	—	86
15			0.05	—	—	86
16			0.09	—	—	86
17			1.1	430	470	86
18			0.2	—	—	86
19			0.2	—	—	86
20			0.6	—	—	85
21			0.61	380	430	84
22			0.75	440	460	84

* Intrinsic viscosity.

However, the thermal stability of such a polymer is considerably poorer than that of the polyoxa-3,4-diazole of analogous structure.

Overberger and Fujimoto[94] obtained polymers containing oxazole *N*-oxide groups by the polymerisation of terephthalonitrile oxide. The copolymerisation of terephthalonitrile oxide with terephthalonitrile leads to the formation of polyoxa-2,4-diazoles:

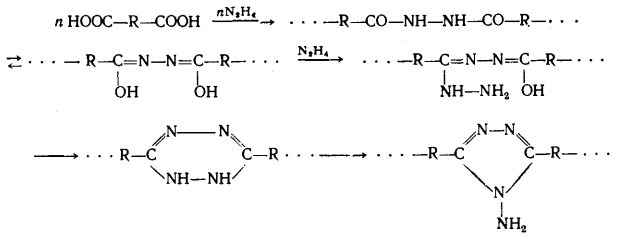


VII. POLYTRIAZOLES

There is a large published literature, consisting mainly of patents, on the synthesis of aliphatic polytriazoles.

In 1941 Prichard[95] described fibre-forming polymers obtained from dihydrazides of dicarboxylic acids. He was the first to point out the difference between the two reactions taking place on heating a salt of hydrazine and a dicarboxylic acid (equimolecular proportions of hydrazine and the acid) and on heating a dihydrazide of a dicarboxylic acid, i.e. 2 moles of hydrazine and 1 mole of the acid. Prichard suggested that in the latter case the polymer contains 1,2,4-triazole-4-amine rings. His work served as a basis for several investigations in this field, conducted during recent years by Moncrieff, Fisher, and their coworkers in England, and by Korshak, Chelnokova, and Shkolina in the USSR.

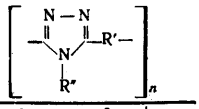
In the view of Fisher et al.[96] the formation of poly-1,2,4-triazole-4-amine can be represented by the scheme

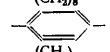
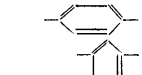
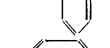
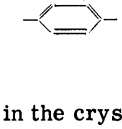
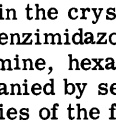


Polyaminotriazoles will not be discussed in detail in the present review, since the synthesis, the properties, and the applications of these polymers have been subjects of detailed consideration in the literature[97-100].

Table 6 gives the chief properties of homopolytriazoles of various structures. Korshak et al.[27] obtained also mixed poly-1,2,4-triazole-4-amines, which exhibit rather better solubility than do the homopolymers. These workers found that polyaminotriazoles are not subject to degradative exchange processes due to interchain exchange reactions.

TABLE 6. Polytriazoles of general formula



Polymer No.	R′	R″	Reduced viscosity in cresol, dl g^{-1}	Temperature, °C: melting	Temperature, °C: start of decomp. in N_2	Ref.
1	$(CH_2)_4$	—H	>0,5	220		101
2	$(CH_2)_8$	—H		180—240		102
3		—H				103
4	$(CH_2)_2$	—NH_2		360		96
5	$(CH_2)_3$	—NH_2	0.62	137—141		99
6	$(CH_2)_4$	—NH_2		300		104
7	$(CH_2)_5$	—NH_2		260		104
8	$(CH_2)_6$	—NH_2	0,4	300—315		99
9	$(CH_2)_7$	—NH_2	0,58	248—225		99
10	$(CH_2)_8$	—NH_2	0,91	225—260		99
11	$(CH_2)_9$	—NH_2				105
12	$(CH_2)_{10}$	—NH_2		245		105
13	$(CH_2)_{18}$	—NH_2	0,72	225—228	—	99
14	$(CH_2)_{20}$	—NH_2	0,83	210—213	—	99
15	$(CH_2)_2S(CH_2)_3$	—NH_2	—	150—155	—	106
16	$(CH_2)_4S(CH_2)_4$	—NH_2	—	160—165	—	106
17	$(CH_2)_5S(CH_2)_5$	—NH_2	—	206—208	—	106
18	$(CH_2)_2SO_2(CH_2)_3$	—NH_2	—	208—210	—	95, 106
19	$(CH_2)_4SO_2(CH_2)_4$	—NH_2	—	258—260	—	95, 106
20	$(CH_2)_5SO_2(CH_2)_5$	—NH_2	—	220—225	—	96, 106
21	$(CH_2)_2O(CH_2)_nO(CH_2)_2$	—NH_2	—	oil	—	107
22		—NH_2	—	—	—	108
23		—NH_2	—	—	—	108
24		C_6H_5	2.0 (HCOOH)	290—310	512	109
25		C_6H_5	2.0 (HCOOH)	240—250	512	109

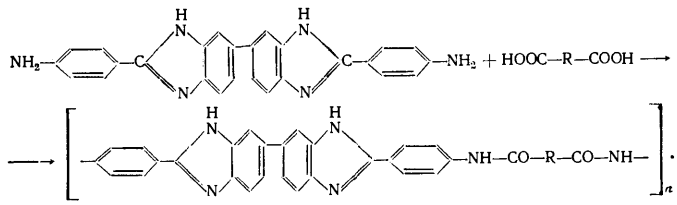
VIII. COPOLYMERS WITH AZOLE RINGS

Copolymers containing azole rings which have been described in the literature can be divided into two groups—cyclolinear copolymers, e.g. polyamides or polyesters containing benzimidazole rings, and cyclic copolymers, e.g. copolymers containing benzimidazole and pyromellitimide rings in the chain.

In copolymers of the first group several workers wished to combine the thermal stability characteristic of polyazoles with adequate solubility and other valuable properties inherent in linear polymers (polyamides, polyesters, etc.). However, the introduction of polyamide and polyester segments produced a substantial diminution in the thermal stability of the copolymers.

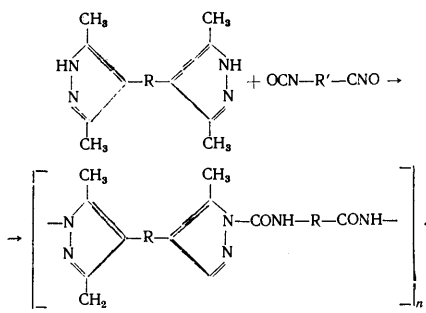
Korshak et al.[110,111] obtained aliphatic poly(amidobenzimidazoles) from diphenyl sebacate, biphenyl-3,3′,4,4′-tetra-amine or diphenylmethane-3,3′,4,4′-tetra-amine, and hexamethylenediamine. The melting point of the copolymers varied with the relative proportions of the initial diamine and the tetra-amine, passing through a minimum at 164°C in the case of biphenyl-3,3′,4,4′-tetra-amine. Increase in the polyamide content is accompanied by an increase in the crystallinity of the copolymers. The synthesis of benzimidazole polyesters from biphenyl-3,3′,4,4′-tetra-amine, hexane-1,6-diol, and diphenyl sebacate is accompanied by secondary reactions, which impair the properties of the final copolymer[111].

Iwakura et al.[112] described a series of polyamides obtained in polyphosphoric acid from dicarboxylic acids and a diamine containing benzimidazole rings:



The polyamide based on sebacic acid begins to decompose in air at 250°C whereas those based on aromatic dicarboxylic acids begin to decompose above 400°C.

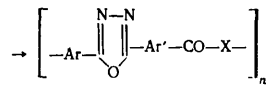
Polyamides containing pyrazole rings were obtained by Korshak et al.[79] by the reaction of dipyrazoles with hexamethylene and methylphenylene di-isocyanates:



These polymers possess viscoelastic properties over the range 200–300°C. They can be regarded as *N*-substituted polyureas. As Fedotova et al.[113] showed, the latter are not very heat-resistant and are amorphous polymers.

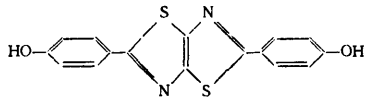
The synthesis of aliphatic polyamides containing triazole rings has been described in several patents and has been reflected in a corresponding review literature[97–100]. Block copolymers of ε-caprolactam and polytriazoles were prepared by Iwakura et al.[101] and later by Grekov et al.[114]

Aromatic polyamides and polyesters of regular structure containing oxadiazole rings have been obtained[104,115] via the corresponding polyhydrazides:



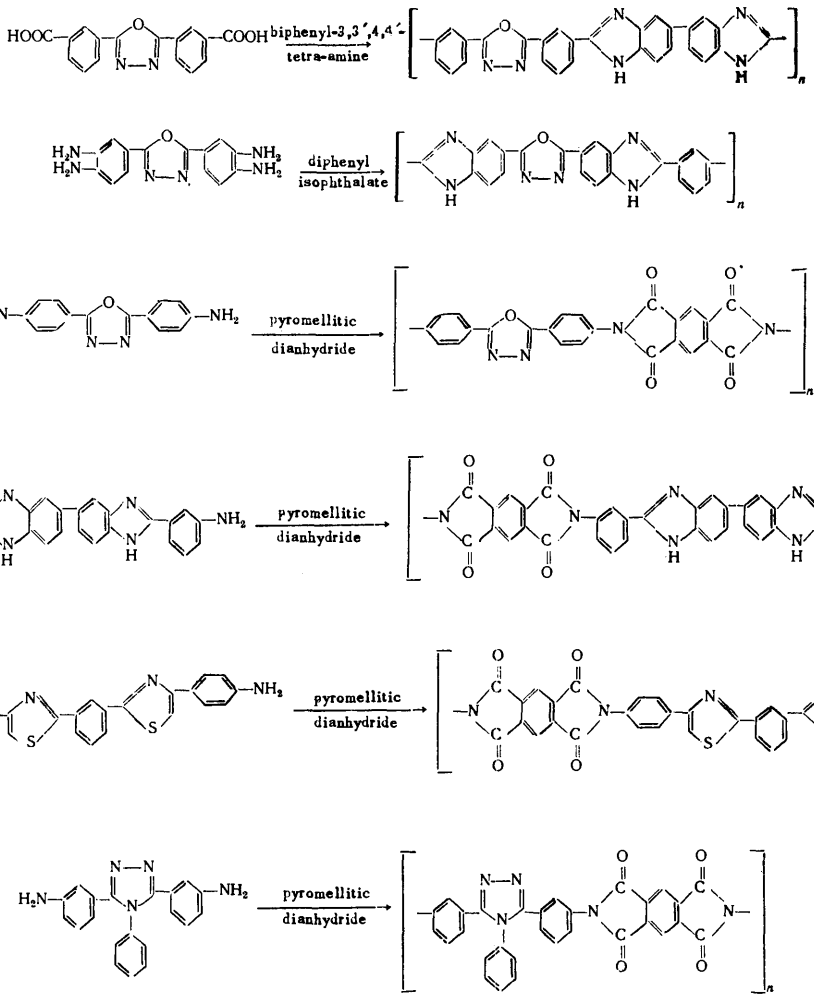
where X = NH or O. The polyamides and the polyesters softened over the ranges 400–470° and 300–400°C respectively.

Fox[116] accomplished the synthesis of various polyesters containing thiazolo[5,4-*d*]thiazole rings using a bisphenol having the structure



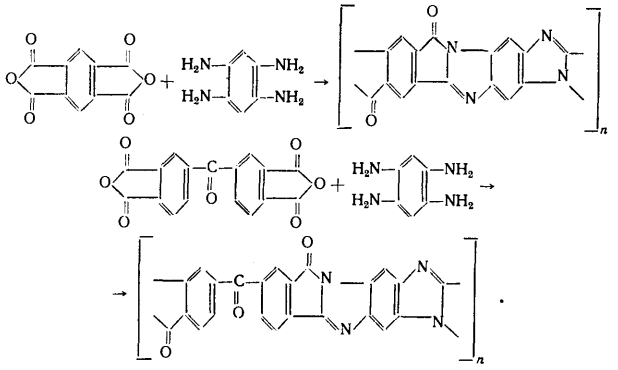
as starting material. When such a bisphenol is treated with carbonyl chloride or a bischloroformate, polycarbonates are produced, whereas treatment with chlorides of aliphatic dicarboxylic acids yields polyesters.

It is probable that the preparation of copolymers of the second group, containing different rings in the chain, will be more effective in preserving the thermal stability of the polyazoles. Unfortunately, very little work has been done in this field, so that it is difficult to reach final conclusions. However, a paper by Preston and Black[117] already substantiates this hypothesis. These workers prepared heterocyclic copolymers of ordered structure, the synthesis of which can be represented schematically as:



These copolymers are extremely thermostable, beginning to decompose in an inert atmosphere at 500–550°C. The authors did not examine other properties of the copolymers.

Adrova [118] reported the synthesis of copolymers containing benzimidazole and benzophosphorimidazoline rings. In the second group of copolymers can be included also the polyimidazopyrolones (polybenzimidazolimides, pyrrones) obtained [5] from aromatic tetra-amines and aromatic dianhydrides:



However, the properties of such polymers are influenced predominantly by the ladderlike or partly ladderlike structure.

IX. GENERAL PROPERTIES OF POLYAZOLES

At the present time the study of polyazoles has been concerned mainly with developing the synthesis of polymers having sufficiently high molecular weights, and considerably less attention has been paid to the properties of these polymers.

1. Chemical Properties

(a) Hydrolytic stability. Polyazoles are characterised by excellent resistance to hydrolysis, as a consequence of the presence of a stable aromatic heterocycle in the macromolecule. There are indications of hydrolytic stability and resistance to the action of acids and alkalis in such polymers as polybenzimidazoles [17,20], polybenzothiazoles and polybenzoxazoles [29], polyoxadiazoles [85], polythiazoles [71], aliphatic polyaminotriazoles [98,99], and polyphenyltriazoles [109].

Vogel and Marvel [17] showed that heating poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazolyl in 70% sulphuric acid produces only a slight diminution in the reduced viscosity. There is practically no hydrolysis when this polymer is boiled in 25% alkali solution for 10 h. Imai et al. [29] made an analogous investigation on polybenzoxazoles and polybenzothiazoles (Table 7). They found that polybenzoxazoles were less resistant to hydrolysis than were polybenzothiazoles, while the latter were less resistant than the corresponding polybenzimidazoles.

The chemical resistance of the polybenzimidazole based on biphenyl-3,3′,4,4′-tetra-amine and sebacic acid has been examined in some detail [20]. It is seen from Table 8 that no significant decrease in the weight of the specimens is produced by either hydrochloric acid or alkali. This indicates that the polymer is stable to acid and alkaline hydrolysis.

TABLE 7. Change in reduced viscosity of polymers as a result of hydrolysis in 5 *N* KOH or 10 *N* H_2SO_4 at 120°C for 5 h.

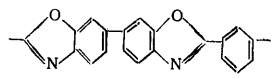
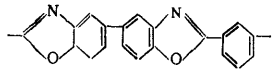
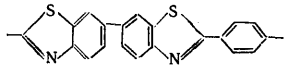
Structural unit	Hydrolysis		
	before	acid	alkaline
	1.50	0.44	0.76
	2.09	0.32	1.01
	1,02	0.61	0.97

TABLE 8. Chemical resistance of poly-2,2′-octamethylene-5,5′-bibenzimidazolyl.

Reagent	Concn. of reagent, %	Conditions		Initial polymer		Polymer after degradation	
		temp., °C	time, h	wt., g	η_{red} in HCOOH	wt., g	η_{red} in HCOOH
HCOOH	90	65	3	—	3.62	—	3.54
HCOOH	90	65	10	—	3.62	—	3.28
HCOOH	90	100	3	—	3.62	—	3.46
HCOOH	90	100	10	—	3.62	—	3.78
HCl	38	180	3	0,25	4.12	0.27	3.16
HCl	38	180	3	0.21	4.32	0.25	2.90
KOH	30	100	10	0,50	3.50	0.50	3.62
$HOOC(CH_2)_8COOH$	100	250	3	—	3.50	—	0.86
$H_2N(CH_2)_6NH_2$	100	190	3	—	3.50	—	2.88

Among all the polyazoles only the polybenzoborimidazolines [43,44] have proved to be unstable to hydrolysis, owing to the peculiarity of the borazole ring. With the polymer obtained from biphenyl-3,3′,4,4′-tetra-amine and tetra-acetyl diborate, for example, the intrinsic viscosity decreased to almost one-third after keeping over water in a desiccator for a week.

The results on the hydrolytic stability of the polyazoles show that it is determined primarily by the nature of the azole ring in the polymer.

(b) Resistance to other chemical reagents. Korshak et al. [27], in a study of polyaminotriazoles, referred to the exceptional stability of the azole ring towards various degradative agents. When two different polyaminotriazoles were heated together for a long time, no exchange reactions were detected, such as are characteristic of other classes of heterochain polymers [119–121].

The solubility of polyazoles in a narrow range of solvents (predominantly of polar type) governs their resistance to oils and organic solvents, but the literature contains no actual papers on this.

Copolymers of polyazoles of the first group will probably have considerably poorer chemical stability than have polyazoles or copolymers of polyazoles of the second group. Thus polyesters containing oxadiazole rings, unlike polyoxadiazoles, are decomposed by the action of sulphuric acid [122].

(c) Stability to heat and oxidation. The thermal stability of polyazoles has been assessed by the

method of thermogravimetric analysis. Although certain differences are possible between results obtained by different workers, caused by different experimental conditions, e.g. different rates of heating, this method is sufficiently reliable to yield comparative data on the thermal stability of polyazoles. It is seen from Tables 1–6 and Figs. 4–7 that all polyazoles made up of alternating azole and phenylene rings are characterised by approximately the same start of intense decomposition in air in the range 450–600°C, whereas polyazoles containing polymethylene or other aliphatic chains usually decompose in the range 300–400°C.

Several polyazoles (e.g. polybenzimidazoles) containing ferrocene or perfluoromethylene units break down at relatively low temperatures, owing to their structural peculiarities. Thus the poor thermal stability of polyperfluoromethylenebenzimidazoles is due to the ease with which hydrogen fluoride is formed from fluorine in the perfluoromethylene chain and hydrogen in the imidazole ring[48]. Nevertheless, a purely perfluoromethylene molecule, e.g. in polytetrafluoroethylene, possesses excellent thermal stability.

Work on the thermal stability of polymers[123] is based on the "cage" theory. On this theory the thermal stability is determined by the phase state of the polymer, so that it depends on the melting point. However, the results for polyazoles show that this principle is not always valid. Thus polythiazoles based on 2,2′-biphenylylene units melt at 164–265°C, whereas a polythiazole based on 4,4′-biphenylylene units does not melt up to 500°C, although all these polymers start to decompose at the same temperature of 500°C (Table 3).

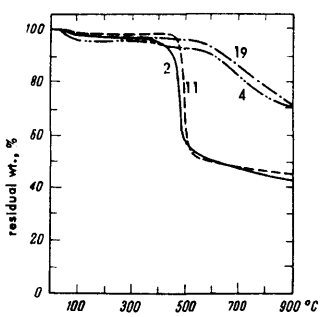


Fig. 4. Thermogravimetric analysis of polybenzimidazoles in air. Numbering of polymers from Table 1.

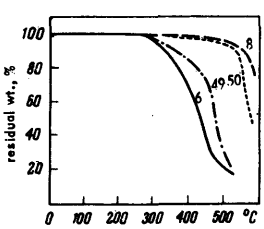


Fig. 5. Thermogravimetric analysis of polybenzothiazoles and polybenzoxazoles in air. Numbering of polymers from Table 2.

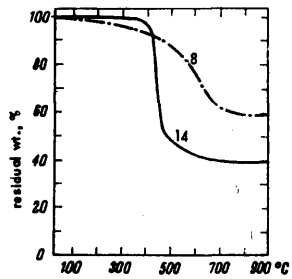


Fig. 6. Thermogravimetric analysis of polythiazoles in air. Numbering of polymers from Table 3.

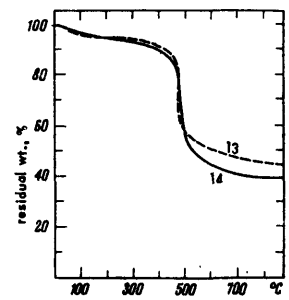
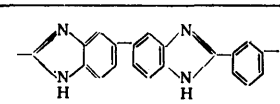
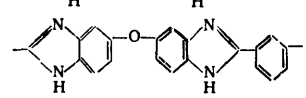
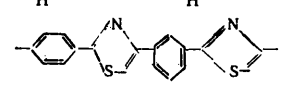
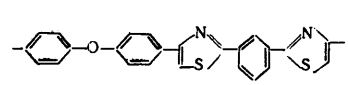
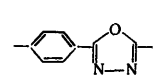
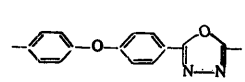


Fig. 7. Thermogravimetric analysis of polyoxadiazoles in air. Numbering of polymers from Table 5.

TABLE 9.

Structural unit	Temp. of start of decomp., °C	Solubility in* DMA	DMF	BA	Remarks
	500	+	×	–	
	500	+	+	+	
	500	–	–	–	does not form films or fibres
	450 (in N_2)	–	–	–	forms stable films
	450	–	–	–	
	430	+	×	–	forms films and fibres from soln.

* DMA = dimethylacetamide; DMF = dimethylformamide; BA = benzyl alcohol.

2. Physical Properties

Solubility. The problem of the thermal stability of polyazoles is closely linked with the preparation of polymers having satisfactory mechanical characteristics and sufficient solubility for goods to be manufactured from them. Polyazoles containing alternating azole and phenylene units often exhibit inadequate mechanical strength and solubility. Therefore various groups are introduced into the polyazole molecule which, without significantly lowering the thermal stability, increase the flexibility of the chain or produce an internal plasticising effect. The introduction of ether links between the phenylene units has proved to be the most successful. Table 9 gives data showing the effect of an oxygen bridge on the properties of polyazoles.

With the polybenzoxazoles as example Korshak et al.[60] showed that the introduction of bulky substituents into polymer molecules considerably improves their solubility. Such polybenzoxazoles dissolve in many organic solvents—chloroform, tetrachloroethane, tricresol, benzyl alcohol, pyridine, dimethylformamide, etc.—while possessing high thermal stability. The solubility is improved also by preparing mixed polymers, but the effect is rather smaller than with linear heterochain polymers, e.g. polyamides. Thus a polyaminotriazole based on sebacic and azelaic acids has a maximum solubility in ethyl alcohol of 8%,[27] and a polyamide based on hexamethylenediamine and the same acids is 100% soluble[124], whereas homopolyaminotriazoles and homopolyamides based on these acids are insoluble in alcohol.

X. USES OF POLYAZOLES

The chief property determining the use of polyazoles is their exceptional thermal stability. In this connection it must be borne in mind that aromatic polyazoles are more promising than aliphatic polyazoles in this respect, although the mechanical properties of the latter are better.

The first striking results on the application of aromatic polyazoles were achieved in the use of polybenzimidazoles as high-temperature and constructional adhesives, coatings, high-temperature fibres, thermal insulation, and binders for glass plastics[122,125-131].

Marvel[8] reported the fibre-forming and film-forming properties of the polybenzimidazole from biphenyl-3,3',4,4'-tetra-amine and diphenyl isophthalate. The unoriented film obtained from a solution of the polymer is dimethyl sulphoxide exhibited at 25°C the properties—tensile strength 0.7 g denier^{-1}, elongation 7%, modulus 35 g denier^{-1}—the corresponding values at 200°C being 0.5, 9%, and 15 respectively. After some orientation, filaments obtained from the solution had a strength of 4.5 g denier^{-1}, which they maintained in air up to 300°C.

Aliphatic polybenzimidazoles possess, together with adequate thermal stability, excellent mechanical properties, which enables them to be used for films, fibres, adhesive compositions, and other purposes. Thus the isotropic film from 2,2'-octamethylene-5,5'-dibenzimidazolyl possesses a tensile strength of 1200–1300 kgf cm^{-2}, an elongation of 18–20%, and good dielectric characteristics. On orientation the strength of the film reaches 5000 kgf cm^{-2}.[132]

It has been stated[65,133] that imidazole polymers can be used as semiconductor materials.

Reports have appeared recently of the use of other aromatic polyazoles. This applies primarily to polyoxadiazoles[134,135], from which it has proved possible to obtain a fibre having excellent thermal stability, chemical resistance, and good mechanical characteristics. The properties of the fibre do not change up to 200°, and only 40% loss in strength occurs at 300°C.

Holsten and Lilyquist[109] showed that polytriazoles also yield excellent thermostable filaments and films. This was to be expected, since aliphatic aminotriazoles have long been known as excellent fibre-forming materials.

The large amount of work which has been done on the structure of polythiazoles[71,73] has enabled products to be obtained having satisfactory mechanical properties and great thermal stability, suitable for the manufacture of films and fibres.

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POLYMERS BASED ON FERROCENE

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I. INTRODUCTION

Ferrocene is the most accessible and stable—and hence the most thoroughly investigated—representative of a novel type of organometallic compound. Several detailed reviews[1-3] have appeared on ferrocene and its derivatives. The aromatic character of ferrocene, its structural peculiarities, the high reactivity, and the thermal stability—unusual for organometallic compounds—have attracted the attention of many research workers, and explain the attempts to use various of its derivatives for the synthesis of polymers.

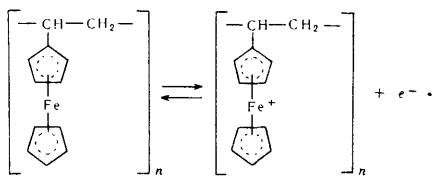
Some hundred different ferrocene-containing polymers are already known, but there has not yet been a thorough review covering this new and fairly extensive field of polymer chemistry. There has merely been mention of certain polymers of ferrocene in reviews by Haiduc on coordination polymers[4] and by Korshak[5] and by Brown[6] on organoelementary macromolecular compounds. Reviews appeared in 1966 by Zimakova[7] and by Zelenetskii[8], but these do not cover completely the vast amount of information on the chemistry of ferrocene polymers.

Ferrocene-containing polymers can be divided into three groups depending on whether they are obtained by polymerisation, polyrecombination, or polycondensation.

2. FERROCENE POLYMERS OBTAINED BY POLYMERISATION

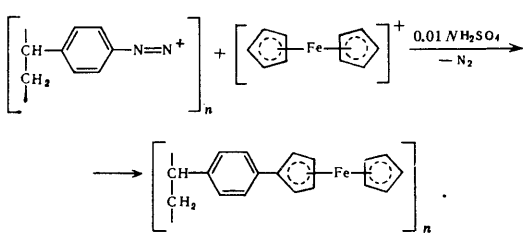
The first polymer of this type, polyvinylferrocene, was prepared from vinylferrocene by Arimoto and Haven[9] in 1955. In the presence of 85% phosphoric acid or potassium persulphate, a viscous oil, soluble in benzene, was formed. When azoisobutyronitrile was used, vinylferrocene polymerised at 80°C to form a benzene-soluble solid melting at 280–285°C. Copolymers of vinylferrocene with methyl methacrylate, styrene, and chloroprene were also obtained[9,10]. All the polymers were soluble in benzene and insoluble in methanol. Clear, brittle films could be obtained from solutions of the solid polymers.

Table 1 lists some properties of homopolymers and copolymers of vinylferrocene. Treatment of the copolymers with formaldehyde yields cross-linked products having redox properties:



Solid polymers of vinylferrocene also possess redox properties, though polyvinylferrocene is insoluble in the solvents normally used for potentiometric titration.

The electron-exchange properties of polyvinylferrocene were studied by sulphonating it in the ring[11]. Analysis showed that two sulpho-groups entered the ring linked by the polymer chain, and one entered the second ring. Sulphonated polyvinylferrocenes are soluble, but they cannot be titrated owing to their rapid decomposition. A further electron-exchange resin, a ferrocene–polystyrene analogue of a redoxite[12], has been obtained from ferrocene:



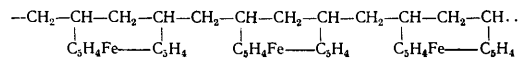
Rausch and Coleman[13] described various copolymers based on ferrocene β-styryl ketone [cinnamoylferrocene], which was synthesised in 81.5% yield from cinnamoyl chloride and ferrocene by the Friedel–Crafts reaction. The

TABLE 1. Homopolymers and copolymers of vinylferrocene.

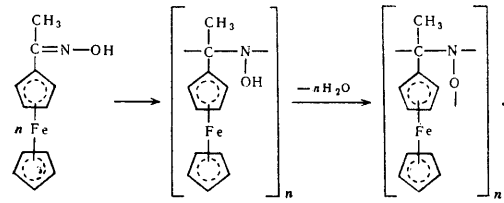
Catalyst	Comonomer	Product	M.p., °C
85% Orthophosphoric acid	—	viscous oil	—
Potassium persulphate	—	oil	—
	—	solid	280—285
Azoisobutyronitrile	methyl methacrylate	solid	190—210
	styrene	solid	158—165
Potassium persulphate	chloroprene	elastomer	—

ketone itself does not polymerise, but it forms copolymers with many vinyl and diene compounds, such as styrene, acrylonitrile, acrylates, butadiene, and isoprene[14,15]. Copolymers with vinyl monomers have been obtained by block polymerisation in the presence of benzoyl peroxide, or by polymerisation in benzene solution (in the absence of thiophen) or in dimethylformamide with azoisobutyronitrile as initiator. Copolymers with dienes were obtained by emulsion polymerisation using dodecanethiol as modifier. These copolymers were coloured powders, elastic materials, or solids melting at 130–275°C.

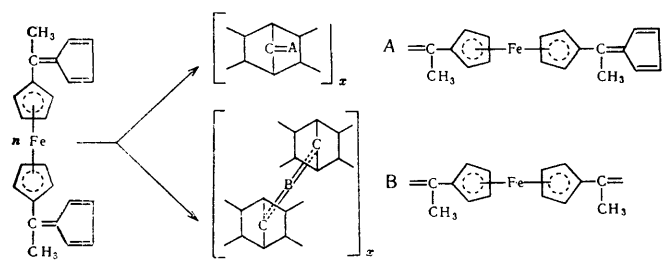
Knox and Pauson[16] attempted to prepare divinyl- and dibutadienyl-ferrocenes via the fulvenes, but were unable to isolate these derivatives, since they underwent rapid polymerisation. The polymer formed from these ferrocenes may have the structure



Ferrocene-containing polymers are formed also by the polymerisation of acetylferrocene oxime and 1,1′-bis-(1-cyclopentadienylidene-ethyl)ferrocene. The oxime undergoes polymerisation at or above its melting point to produce an almost quantitative yield of insoluble polymers[17]:



The thermal, catalytic, and radiation polymerisation of the difulvene is represented by the scheme[17]



Thermal polymerisation was conducted in sealed tubes at various temperatures for 1–8 h. Insoluble and infusible polymers were produced above 150°C. Polymerisation of the difulvene derivative in the presence of benzoyl peroxide in dioxan solution after 8 h yielded 28.2% of polymers having a linear structure and 9.1% of cross-linked polymers (with 2% of benzoyl peroxide at 65°C). With 3% of the peroxide at 100°C the polymerisation was almost quantitative.

The copolymerisation of ferrocene with hexamethylene di-isocyanate gave a 73% yield of an infusible copolymer, a polyferrocenylenepolyamide, which was insoluble in the usual organic solvents[17]. This copolymer results from the addition of ferrocene hydrogen atoms to the isocyanate groups, which suggests that these atoms are very mobile in comparison with the hydrogen atoms in benzene, for the latter does not react with di-isocyanates. The elementary composition and the infrared spectra of the copolymer indicate that it has the structure

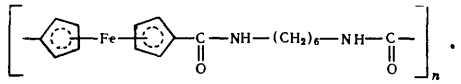
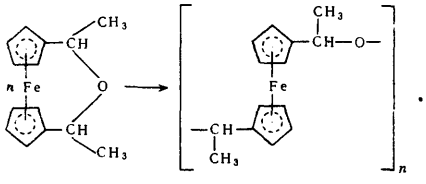
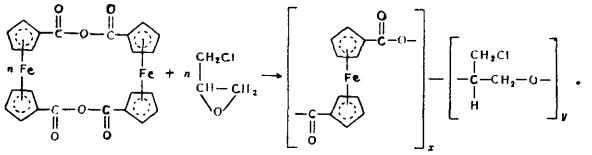


Table 2 lists the characteristics of the above ferrocene-containing polymers, obtained by the polymerisation of acetylferrocene oxime and of 1,1′-bis-(1-cyclopentadienylidene-ethyl)ferrocene, and by the copolymerisation of ferrocene with hexamethylene di-isocyanate.

A recent paper[18] has reported the synthesis, by polymerisation accompanied by ring-opening of ferrocene derivatives containing reactive bridging chains between the two cyclopentadienyl rings, of polymers containing ferrocene in the main chain. Treatment of 1,1′-(1,1′-epoxydiethyl)ferrocene with certain Lewis acids used as catalysts gave a yellow–orange polymeric product. Infrared spectroscopy showed that the polymeric product obtained by polymerisation at room temperature contained ether chains, but that obtained at 75°C did not contain them. The reaction occurred according to the scheme



Copolymerisation has been accomplished[18] also between ferrocene-1,1′-dicarboxylic anhydride and 1-chloro-2,3-epoxypropane, the products being dark brown esters insoluble in the usual organic solvents:



The polymerisation of acryloylferrocene in the presence of various initiators has been studied, as well as the copolymerisation of acrylylferrocene with acrylonitrile[19].

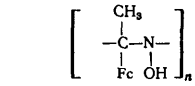
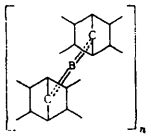
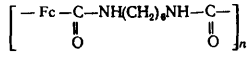
3. FERROCENE POLYMERS OBTAINED BY POLYRECOMBINATION

Polyrecombination is distinguished fundamentally from polymerisation by the fact that the starting materials are saturated compounds and that it is a stepwise reaction—not a chain reaction—although it occurs by a radical mechanism. Polyrecombination consists in treating a hydrocarbon with a peroxide, e.g. with t-butyl peroxide in an atmosphere of nitrogen at 200°C. The t-butoxyl and methyl radicals resulting from breakdown of the peroxides abstract hydrogen from the ferrocene (or α-hydrogen from its alkyl substituent), and the radicals thus formed recombine among themselves to form a polymer[20].

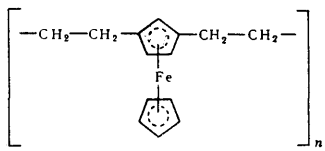
In 1958 Korshak et al. were the first to use polyrecombination to obtain a ferrocene-containing polymer based on a homoannular di-isopropylferrocene[21]. Later they made a detailed investigation of the polymer[22]. Its synthesis was conducted at 170°C with equimolecular proportions of peroxide and monomer. The polymer was a reddish powder, soluble in benzene and chloroform, with molecular weight 8200 and melting point 155–180°C.

Polyrecombination was used to obtain polymers (polyferrocenylenes) from ferrocene itself[20,23–25]. Formation of a linear polyferrocenylene, readily soluble in benzene, was accompanied by that of an insoluble polymer, probably possessing a cross-linked structure. The two polymeric forms were separated by treating the reaction mixture

TABLE 2. Characteristics of some ferrocene-containing polymers obtained by polymerisation.

Structure of polymer	Method of polymerisation	Elementary composition, wt. %								Characteristic absorption bands, cm^{-1}
		C		H		Fe		N		
		found	calc.	found	calc.	found	calc.	found	calc.	
	thermal	59.17	59.25	4.99	5.3	24.01	23	4.69	5.75	818, 1000, 1100, 1426, 1603
	thermal	77.85	78.6	6.14	6.01	15.1	15.3	—	—	820, 1370, 1436
	catalytic	77.91	78.6	6.16	6.01	14.9	15.3	—	—	1586–1700
	radiation	77.18	78.6	6.18	6.01	14.55	15.3	—	—	
	thermal	61.5	61.1	6.72	6.20	15.25	15.8	7.2	7.9	814, 1000, 1100, 1360, 1450, 1670

with benzene. The soluble polyferrocenylenes had molecular weights of 370–7000 and softening points of 290–300°C. The insoluble polyferrocenylene softened at 400°C, which probably indicates that cross-linkages between the chains were comparatively rare. The structure of the polyferrocenylenes, and also of the polymers obtained by the polyrecombination of di-isopropylferrocene, is supported by the infrared spectra, which contain absorption maxima, characteristic of a free cyclopentadienyl ring, in the region of 820, 1000, and 1100 cm^{-1}. On this basis the soluble polymers probably have the structure



(I).

Refinement of the polymer structure (I) permits it to be regarded as a chain of ferrocene structures linked by methylene bridges formed as a result of preliminary methylation of the ferrocene.

The work of Korshak, Sosin, and other Soviet investigators on the preparation of polyferrocenylenes by polyrecombination in the presence of t-butyl peroxide has been repeated by foreign workers [26], who have obtained under carefully controlled reaction conditions soluble polymeric compounds comparable in molecular weight and physical properties with those obtained earlier. However, the elementary composition of the products differs from that calculated for polyferrocenylenes. Spectroscopic examination and determination of the elementary composition, confirmed by the isolation not only of bi- and ter-ferrocenyl but also of diferrocenylmethane and diferrocenylmethyl t-butyl ether, substantiated the Soviet authors' results indicating that the compounds obtained were polymeric chains comprising polyferrocene segments linked by methylene and other aliphatic groups. These bridging groups result from methylene and t-butyl radicals.

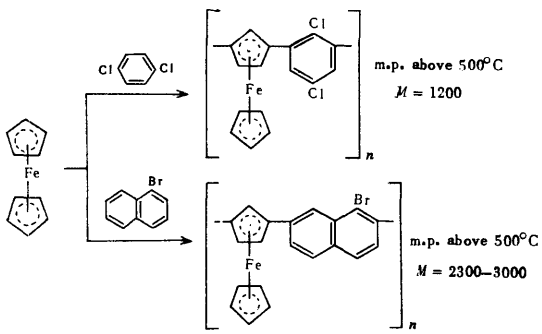
The polyrecombination of various alkyl derivatives of ferrocene was studied [27]. Polymers were obtained based on isobutylferrocene, di-isobutylferrocene, isopentylferrocene, and cyanoferrocene, as well as copolymers of ferrocene with isobutylferrocene, stilbene, and dimethyl dodecanedioate. The polyrecombination was conducted at 200°C, the molar ratio of t-butyl peroxide to the initial compound being 1.2 : 1. The alkylferrocene polymers were dark yellow and brown powders of molecular weight 3000–9000. The infrared spectra of soluble polymers exhibited in all cases absorption maxima in the region of 1000 and 1100 cm^{-1}, which are characteristic of free cyclopentadienyl rings. Hence only one of the cyclopentadienyl rings was involved in polymer formation in the above cases.

Electron spin resonance (e.s.r.) and a positive magnetic susceptibility were observed with these polymers [20,28]. However, further investigation showed [29] that the anomalous magnetic properties of ferrocene polymers were entirely due to the presence of paramagnetic and ferromagnetic impurities. Specially purified specimens of the above ferrocene polymers gave no e.s.r. signal.

The effect of preliminary heating in a vacuum at 200° and 270°C was studied on the electrical and magnetic properties of polyferrocenylenes obtained by polyrecombination [30]. Heating the polymers in a vacuum at 270°C results in a substantial change in their physical properties. The electrical resistance and the activation energy E_σ diminish appreciably, and a break appears on the conductivity–temperature straight lines. The magnetic susceptibility of polymers which have been heated in a vacuum at 270°C is much higher than that of the unheated polymers (by factors of 10^2–10^3). A marked dependence of χ on the magnetic field strength H appears, which is characteristic of ferromagnetic substances, χH exhibiting a saturation effect at the fields used. The appreciable ferromagnetism of ferrocene polymers which have been compressed and heated in a vacuum is due to the ferromagnetic properties of organometallic compounds of iron, although the possibility of thermal decomposition of the polymer with the formation of ordinary ferromagnetic compounds of ferrocene cannot be completely excluded with the preparations studied.

Paushkin, Vishnyakova, and their coworkers [31–34] investigated the polyrecombination of various alkylferrocenes and the copolyrecombination of ferrocene with 1-bromonaphthalene, *p*-dichlorobenzene, benzonitrile, salicylic acid, salicylaldehyde, benzaldehyde, phthalic anhydride, and other aromatic compounds. The reaction was conducted in the presence of various amounts of t-butyl peroxide at 175–200°C.

Copolyrecombination yields products of the following types:



Soluble (dark brown) and insoluble (black) solid polymers were obtained. The experimental results and the characteristics of the products are given in Table 3. All the specimens show a positive temperature coefficient of conductance, and the dependence of conductance on temperature is exponential in character.

4. FERROCENE POLYMERS OBTAINED BY POLYCONDENSATION

Nesmeyanov and Kochetkova prepared polymers by the polyalkenylation of ferrocene with 1,2-dichloroethane and dichloromethane in the presence of aluminium chloride at the boiling point of dichloroethane [20,28,35,36]. Interaction of ferrocene with a large excess of 1,2-dichloroethane under severe conditions in the absence of a foreign solvent yielded a series of "pentaethanopolyferrocenes" not containing halogen, soluble in chloroform and benzene and insoluble in methanol, instead of the diferrocenylethane and resins of relatively high molecular weight obtained previously [37], in which several ferrocene units were linked by CH_2–CH_2 bridges. The products obtained differed among themselves in their solubility in ether, this property being utilised for their separation. On the basis of elementary analysis the substance of lowest molecular weight, which

TABLE 3. Characteristics of ferrocene-containing polymers obtained by polyrecombination.

Initial compound (Fc = ferrocene)	Molar ratio peroxide : initial compound	Yield of polymers based on initial cpd., wt. %		Mol. wt. of soluble polymer	Melting point, °C		ΔE, eV	σ^*_{50}, ohm^{-1} cm^{-1}
		sol.	insol.		sol.	insol.		
Fc + 1-bromonaphthalene	1.36:1	5.4	23.0	2300—3000	>500	>500	0.54	$2.5 \cdot 10^{-13}$
ditto	3:1	6.6	26.0		—	—	0.54	$1.7 \cdot 10^{-13}$
Fc + *p*-dichlorobenzene	1. 6:1	5.2	23.0	1200	>500	>500	0.47	$2.83 \cdot 10^{-10}$
ditto	3:1	4.2	32.9	—	—	—	0.58	$2.5 \cdot 10^{-12}$
Fc + benzonitrile	2:1	none	27.0	—	—	>500	—	—
Fc + salicylic acid	1. 8:1	none	77.0	—	—	>500	0.33	$4.0 \cdot 10^{-9}$
Fc + salicylaldehyde	1. 5:1	3.3	35.7	—	—	>500	0.45	$3.7 \cdot 10^{-12}$
Fc + benzaldehyde	2 :1	none	34.8	—	—	>500	—	—
Monoisobutylferrocene	2 :1	39.0	none	2300	300	—	—	—
Monoisopentylferrocene	2 :1	35.5	none	1300	290—295	—	—	—
Monoiso-octylferrocene	2 :1	34.0	none	2000	290	—	—	—
Fc + naphthalene	2 :1	15.35	18.25	3000	260—270	310—320	—	—
Fc + benzophenone	1.64:1	7.0	23.0	1100	180—190	320—330	—	—
Fc + azobenzene	2 :1	13.7	none	—	>500	—	—	—
Fc + benzoic acid	1.76:1	6.55	71.3	—	> 260	>500	—	—
Fc + phthalic anhydride	1.66:1	none	30.7	—	—	>500	0.036	

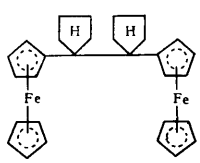
* Electrical properties given for the insoluble polymers.

decomposed at 130°C, was regarded as a pentaethanodiferrocene, containing two ferrocene units and five ethano-bridges. The products of molecular weight 1000–2000, which were less soluble in ether, contained 4–8 ferrocene residues. Their analyses were close to that of the previous substance. This suggested that they had an analogous structure.

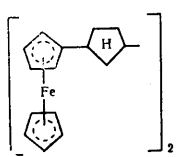
Nesmeyanov et al.[38] obtained acetyl derivatives of "pentaethanodiferrocene". The acylation of this compound with acetic anhydride in the presence of 85% phosphoric acid gives a monoacetyl derivative. Acylation with acetyl chloride in the presence of anhydrous aluminium chloride in dichloromethane (solvent) yields "diacetylpentaethanodiferrocene" and other "polyacetylpentaethanodiferrocenes". The formation of a diacetyl product confirmed the presence of two acylatable cyclopentadienyls.

In a brief communication Goldberg[39] mentioned the possibility of obtaining a substance with the same properties as "pentaethanodiferrocene" by the action of aluminium chloride on ferrocene in benzene solution in the absence of dichloroethane.

Further investigations by Nesmeyanov and Kochetkova[40] on the action of aluminium chloride on ferrocene, comparison with the action of anhydrous hydrogen fluoride on ferrocene[41], and an attempt to hydrogenate the resulting "pentaethanodiferrocene" led these workers[40] to the conclusion that their compound was 1,1′-diferrocenylbicyclopentyl

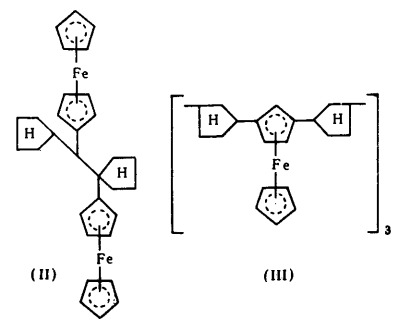


The presence of small quantities of other isomers

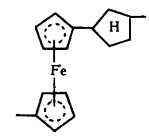


was also possible. However, the substances of molecular weight 1000 and 2000 described previously were probably polymers of cyclopentenylferrocene.

Cottis and Rosenberg[42] were able to separate the compound described earlier as "pentaethanoferrocene" into two parts—a reddish-orange rubberlike substance (II) soluble in ether and partly soluble in methanol, and a yellow solid (III)—



Other workers[43] have studied the action of $ZnCl_2$–H_2O on ferrocene in the absence of any solvent. The reaction was conducted in the melt (at 180°C) with relative proportions of ferrocene : $ZnCl_2$: H_2O = 1 : 0.3 : 0.01. The reaction gave products soluble in hexane, which were separated chromatographically and were shown by analysis to be 1,1′-(cyclopent-1,3-ylene)ferrocene and two isomers of diferrocenylcyclopentane. The product, which was insoluble in hexane but soluble in dioxan, benzene, and chlorinated hydrocarbons, had melting point 125–135°C and molecular weight 2030, and from analysis was an oligomer containing as unit

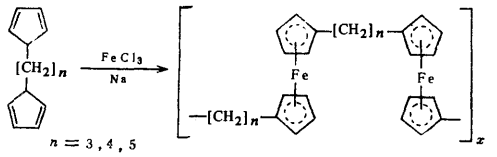


In 1961 Knobloch and Rauscher reported the preparation by interfacial polycondensation of polyamides and polyesters containing ferrocene, the starting materials being ferrocene-1,1′-dicarbonyl chloride and certain diols (2,2-diphenylpropane-*pp*′-diol, quinol, and ethylene glycol) and diamines (ethylenediamine, hexamethylenediamine, piperazine, and *p*-phenylenediamine).[44] The properties of the polyesters and polyamides are listed in Table 4. With the exception of the polymer based on *p*-phenylenediamine,

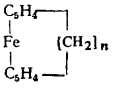
they all dissolve in the usual solvents for polyamides—*m*-cresol and 90% formic acid—and swell in 1,1,2,2-tetrachloroethane, acetone, pyridine, 1,4-dioxan, and tetrahydrofuran. Polymers obtained from hexamethylenediamine dissolve in dimethylformamide, while the polyamide based on piperazine readily dissolves in 1,1,2,2-tetrachloroethane. The polyamide obtained from hexamethylenediamine breaks down at an appreciable rate in formic acid. The molecular weights of the polymers, calculated from viscosities, were 8300–12 000.

Polyurethanes of melting points 91–225°C have been obtained by the polycondensation of ferrocene di-isocyanate with glycols—ethanediol, hexane-1,6-diol, decane-1,10-diol, *p*-phenylenedimethanol, ferrocene-1,1′-diol, and quinol—the polymers being partly soluble in dimethylformamide and dissolving well in formic acid[45].

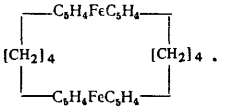
It is theoretically possible to synthesise polymers containing ferrocene in their structure from the disodium derivatives of $\alpha\omega$-dicyclopentadienylalkanes with iron(III) chloride in tetrahydrofuran[46,47]:



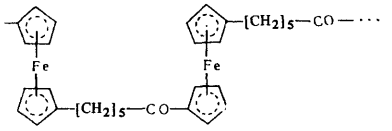
Carrying out this reaction led not only to the production of the polymers but also to the isolation of monomeric ansaferrocenes



and a small amount of cyclic dimers, e.g.

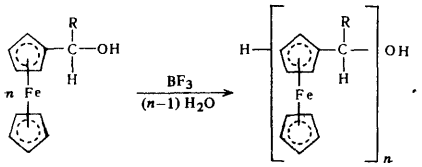


The preparation of polymers having the structure



has also been described[48].

The polycondensation of 2-hydroxyalkylferrocenes yields polymers containing alternating ferrocene and alkyl groups in the main chain[49]:



Formation of a C–C bond, which occurs very readily with the elimination of water, can be explained by the great tendency of these compounds to form ferrocenylcarbonium ions:

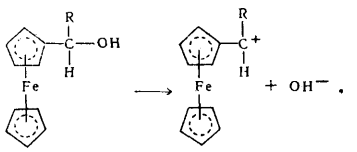


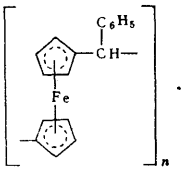
TABLE 4. Properties of polyamides and polyesters obtained from ferrocene-1,1′-dicarbonyl chloride.

Diamine or diol	Organic phase	Base	Duration of reaction, min	Yield, %	[η]	Properties of polymer
Ethylenediamine	toluene	excess of amine	1.0	–	–	–
Ethylenediamine	benzene	excess of amine	2.0	79	0.14	yellow–orange powder, dark at 180°C, brownish and rubberlike at 225°C
Hexamethylenediamine	benzene		2.0	87	0.21	yellow–orange powder decomposing at 110°C, rubberlike at 165°C, dark at 220°C
Piperazine	benzene		3.0	80	0.22	yellow–orange powder, softening at 160°C, transparent at 190°C, orange at 300°C
p-Phenylenediamine	dichloromethane		3.0	93	insol.	brown powder, dark at 230°C, black at 300°C
2,2′-Diphenylpropane-*pp*′-diol	dichloromethane		3.0	70	0.10	orange powder, m.p. 165°C
Quinol	dichloromethane		3.0	63	insol.	brown powder, dark at 200°C

The stability of ferrocenylcarbonium ions has been referred to in other papers[50,51]. By treating ferrocenylmethanol with an acid solution of alumina in benzene Schlögl and Mohar[52] obtained liquid polymers, to which they attributed the above structure (the molecular weight of the products was not stated). The polymer from hydroxybenzylferrocene was a yellow-green powder soluble in the usual solvents, brittle films of which could be obtained from the solution in benzene.

A product, insoluble as a consequence of possible cross-linking, is formed (in 3% yield) by the polycondensation of 1,1′-bis-(1-hydroxyethyl)ferrocene in benzene solution[52]. It is an infusible yellow-green powder, insoluble in the usual solvents, and decomposing at 170–180°C.

Neuse and Trifan[53] studied the polycondensation of ferrocenylmethanols having the structure FcCH(OH)R, where R = H, CH_3, C_6H_5. The polycondensation was conducted in the presence of Lewis acids, the best result being obtained in the presence of zinc chloride, the yield of polymer being 96%. The polycondensation of α-ferrocenylbenzyl alcohol[54] leads to the formation of polymeric ethers of low molecular weight, which in the presence of Lewis acids at elevated temperatures yield products of higher molecular weight having the structure



From 1954 papers began to appear on the condensation of ferrocene with aldehydes in the presence of strong acids (sulphuric, hydrochloric, hydrofluoric) and Lewis acids, leading to the formation of products of low molecular weight (diferrocenylmethane and bisferrocenylphenylmethane) and ferrocene-containing polymers of molecular weight up to 5000. Nesmeyanov and Kritskaya[55] found that ferrocene reacts with aqueous formaldehyde and with benzaldehyde in the presence of concentrated sulphuric acid at 65–70°C, with equimolecular proportions of ferrocene and aldehyde. The total yield of condensation products then reached 65–75% of theoretical. Diferrocenylmethane was obtained, a substance soluble in benzene, chloroform, and dioxan and melting at 191°C, as well as bisferrocenylphenylmethane, soluble in acetone and melting

at 218–220°C. The interaction of ferrocene with benzaldehyde yielded a compound of m.p. 268–270°C, having the composition

$$(C_5H_4)_2Fe[CH(C_6H_5)][CH(OH)C_6H_5]Fe(C_5H_4)(C_5H_5)\ . \qquad (IV)$$

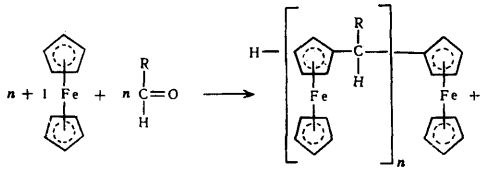
Valot[56] points out that the condensation of ferrocene with formaldehyde in sulphuric acid yields, in addition to diferrocenylmethane and traces of 1,2-diferrocenylethane, a polycondensation product which is a light brown powder of molecular weight 4800, readily soluble in benzene, toluene, and pyridine, sparingly soluble in dimethylformamide, and insoluble in ether and acetone. This product partly darkens at 150°C, and at 170°C is converted into a brownish-red viscous mass. It was proposed[57] that the condensation of ferrocene with formaldehyde and with benzaldehyde should be accomplished in the presence of a large quantity of anhydrous hydrogen fluoride. Analysis suggests that the compound obtained is formed by the condensation of two ferrocene molecules with two aldehyde molecules, accompanied by the elimination of two molecules of water. It is noteworthy that the melting point of this compound corresponds to that of the product (IV) obtained by Nesmeyanov and his coworkers[55].

A considerable quantity of insoluble products were formed by the condensation of ferrocene with benzaldehyde and with formaldehyde in the presence of sulphuric acid and hydrogen fluoride, but these were not isolated or investigated.

The condensation of ferrocene with benzaldehyde has been accomplished also in the presence of 1 ml of concentrated hydrochloric acid in glacial acetic acid at room temperature[58]. The mixture is allowed to stand without stirring for a week, and is then processed. A black powder of indefinite melting point is obtained, its elementary composition corresponding to the empirical formula $C_{17.8}H_{15.3}FeO_{1.4}$. The possibility is mentioned of condensing ferrocene with other aldehydes—such as acetaldehyde, propionaldehyde, butyraldehyde, chloral, *p*-nitrobenzaldehyde, etc.—with ferrocene : aldehyde ratios of 1 : 1–10 and above. The catalysts used are strong acids—phosphoric, sulphuric, hydrobromic, toluene-*p*-sulphonic, hydrochloric, and trichloroacetic—the quantity of which should not exceed 1 part in 10–1000 parts of ferrocene.

The polycondensation of ferrocene with benzaldehyde has been conducted also in the presence of the complex catalyst $ZnCl_2$–HCl(gas) [59] at temperatures ranging from −20° to +140°C.

Neuse and Trifan[60,61] have studied the polycondensation of ferrocene with aldehydes in the presence of Lewis acids (mainly zinc chloride), in amounts of 3–30% on the weight of ferrocene. These workers assume that condensation proceeds via the formation of intermediate ferrocenylmethanols and the corresponding carbonium ions, the final product of the reaction having the structure (V):

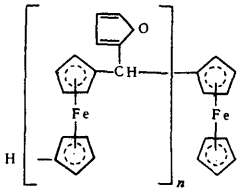


(V)

The condensation was conducted in an atmosphere of nitrogen in an autoclave at 130–180°C. Soluble, readily fusible polymers of molecular weight 2500 were obtained having the structure (V) with R = H, CH_3, C_6H_5; the yield reached 70%. Crotonaldehyde also yields polymers having the structure (V) under the same conditions, but owing to side-reactions at the double bonds in the aldehyde the yield does not exceed 20–30%.

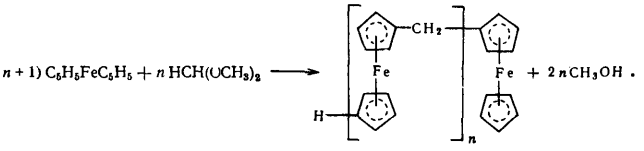
The condensation of ferrocene with furfuraldehyde and with the *o*-methoxy-, *p*-hydroxy-, *p*-carboxy-, and *p*-cyano-derivatives of benzaldehyde at atmospheric pressure gave soluble polymers of molecular weight up to 5000. In these cases the elementary composition differed slightly from that expected for the structure (V), owing to steric and electronic effects of the substituent groups and their tendency to undergo competing side-reactions.

The polycondensation of ferrocene with furfuraldehyde has since been studied in greater detail[62]. Lewis acids were used as catalysts. The molecular weight of the resulting polymers

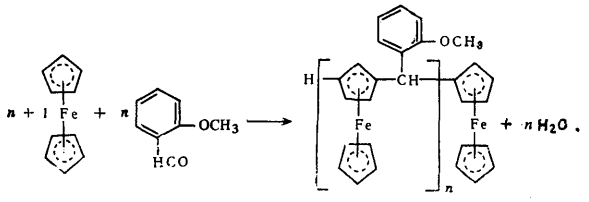


lay within the range 800–4500.

The polycondensation of ferrocene with dimethoxymethane in the presence of zinc chloride at 150–170°C for 8 to 12 h gave a polymer of the structure indicated below[63]:



The polycondensation of ferrocene with anisaldehyde was effected with various proportions of the starting materials in the presence of zinc chloride at 135° and 165°C for 0.9–13 h:[64]

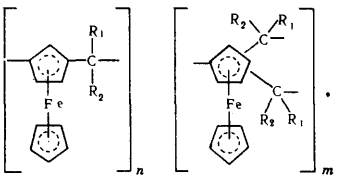


A yield of soluble polymers of 54–78% has been obtained by the polycondensation of ferrocene with *p*- and *o*-formylbenzoic acids, with a molar ferrocene : aldehyde ratio of 0.9 : 3.0, at 115–170°C for 0.4–1.7 h.[65]

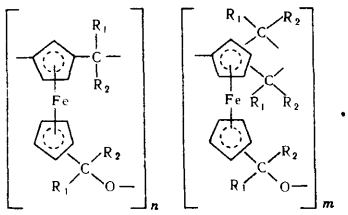
Kotrelev et al.[66] have obtained products of the polycondensation of ferrocene with diazotised benzidine (with various proportions of the starting materials) and of 1,1′-diacetylferrocene with furfuraldehyde. Determinations were made of the thermomechanical properties of the resulting polymers and of their moulding compositions with kaolin.

The polycondensation of ferrocene with various ketones —acetone, butan-2-one, cyclohexanone, acetophenone, and benzophenone—has been studied in the presence of the complex catalyst $ZnCl_2$ + HCl(gas). With relative proportions of ferrocene : ketone = 1 : 2 the yield of ferrocene-containing polymers varied from 29.1% to 76.5%.[67] From

a study of the properties of the polymers it is suggested that with these proportions of the reactants the polycondensation involves the elimination of water, perhaps via intermediate ferrocenylmethanols, with the formation of soluble and insoluble polymers. In the soluble polymers one molecule of ferrocene is associated with 1.5–2 $>CR_1R_2$ groups: i.e. the polymers probably have the structure



On the basis of the elementary analysis the insoluble polymers are assigned the structure

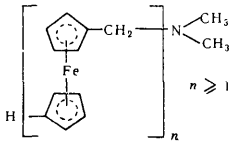


In the absence of ferrocene the condensation of ketones in the presence of $ZnCl_2$ + HCl as catalyst proceeds only as far as formation of dimers and trimers. Addition of 5 mole % of ferrocene to this mixture enhances the activity of the system, so that liquid and solid polymers not containing iron are formed, and also polymeric ferrocene-containing products.

Interaction of ferrocenyl cyanide with ferrocenyl-lithium[68] gives a diferrocenyl ketone in 55–60% yield, and reaction of the latter with ferrocenyl-lithium leads to the formation of triferrocenylmethanol (yield 60%). Reduction of the carbinol with zinc dust in acetic acid gives triferrocenylmethane:

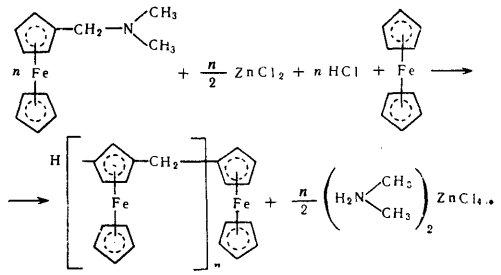
$$C_5H_5FeC_5H_4CN \xrightarrow{C_5H_5FeC_5H_4Li} (C_5H_5FeC_5H_4)_2CO \xrightarrow{C_5H_4FeC_5H_4Li} \rightarrow (C_5H_5FeC_5H_4)_3COH \xrightarrow{Zn+CH_3COOH} (C_5H_4FeC_5H_4)_3CH.$$

The condensation of *NN*-dimethylaminomethylferrocene has also been studied[69,70], in the presence of the $ZnCl_2$–HCl catalytic system in the melt. Polymers



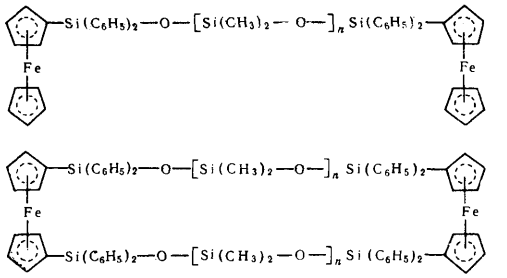
were obtained, containing ferrocenylene structures separated by methylene groups. The products had molecular weights lying in the range 4000–8000. The optimum molar proportions were Mannich base : $ZnCl_2$: HCl = 2 : 1 : 2.

NN-Dimethylaminomethylferrocene has been subjected also[71] to polycondensation with ferrocene:



The structure of the resulting polymer has been confirmed by elementary analysis and the infrared spectra.

The synthesis of several derivatives of ferrocene containing silicon has been described[72]. Various compounds have been obtained containing two ferrocene molecules linked by chains containing silicon atoms

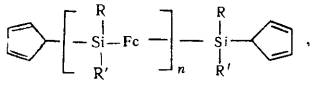


The patent claims[72] that these compounds can be used as lubricants and as defoaming agents for several organic substances.

A series of symmetrical silanylferrocenes—1,1′-bis-(3-phenyltetramethyldisiloxanyl)ferrocene, 1,1′-bis-(5-phenylhexamethyltrisiloxanyl)ferrocene, 1,1′-bis-(7-phenyloctamethyltetrasiloxanyl)ferrocene, etc.—have been obtained. These silanylferrocenes possess good lubricating properties and high thermal stability[73].

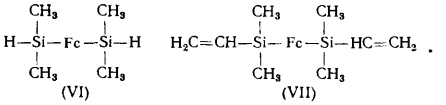
Various unsymmetrical siloxanylferrocene derivatives have also been synthesised[74], by a very complicated multistage method.

The preparation has been described[75] of polymers containing alternating ferrocen-1,1′-ylene and disubstituted silylene groups

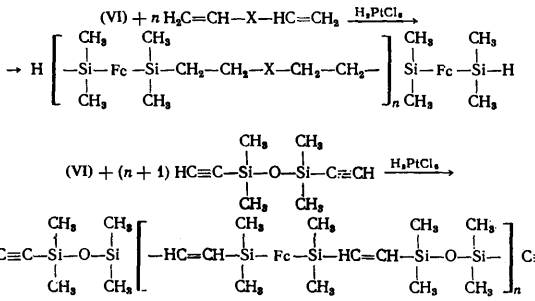


where Fc is a ferrocene residue, and R and R′ are hydrocarbon radicals containing aliphatic, cycloalkyl, aromatic groups and halogenated derivatives, alkoxy-groups, or halogens. These polymers maintain their chemical and thermal stability over a wide range of temperatures.

The reduction of 1,1′-bisethoxydimethylsilylferrocene with lithium tetrahydroaluminate gave a yield exceeding 90% of 1,1′-bisdimethylsilylferrocene (VI), which added acetylene to form 1,1′-bisvinyldimethylsilylferrocene (VII):

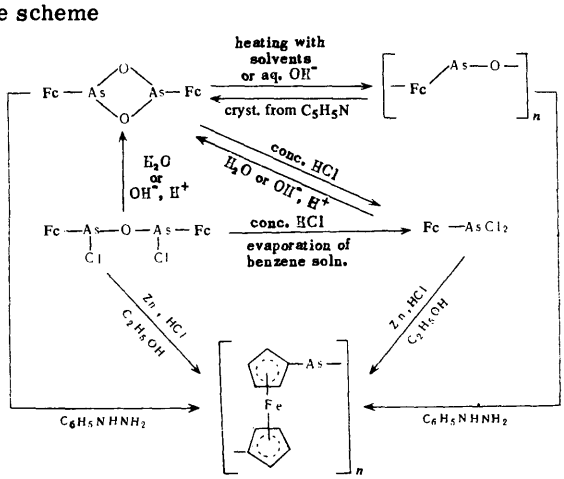


The polyaddition of (VI) to (VII) or to other organosilicon compounds containing two unsaturated terminal groups, and also the addition of (VII) to organosilicon compounds having two $SiHR_2$ terminal groups, lead to the formation of thermostable polymers in which ferrocene is located in the main chain. By varying the proportions of the components it is possible to obtain macromolecules containing two $SiHR_2$ or two unsaturated terminal groups[76]. The reaction proceeds according to the scheme

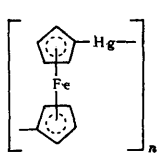


where X = $-Si(CH_3)_2.O.Si(CH_3)_2-$ and Fc = $-C_5H_4FeC_5H_4-$.

Arsenic trichloride[77] gives macromolecular compounds as well as new monoferrocene derivatives of arsenic. The polymers were readily obtained by heating dimeric arsenoferrocene in aqueous alkali, this being explained by thermal hydrolysis of the ferrocenearsonite anion. The conversion of the dimer into a polymer in various solvents is explained by these workers[77] as due to solvolysis of the As–O bond by the solvents. The formation of polymers is represented by the scheme



The synthesis has been described[78] of macromolecular mercury compounds of ferrocene of the type



Products having the composition $(C_{10}H_8FeHg)_x$ were obtained by treating 1,1′-bischloromercuriferrocene with a solution of sodium iodide in a mixture of ether and alcohol or with an aqueous solution of sodium thiosulphate.

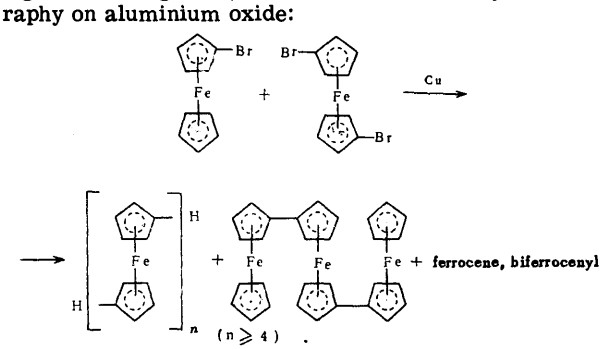
The polycondensation of ferrocene and its derivatives yielded polymers having a system of conjugated double bonds, which possessed semiconductor properties.

Several polyferrocenylenes have recently been synthesised by various methods (besides the polyrecombination reaction described above).

Nesmeyanova and Perevalova[79] obtained ferrocene polymers insoluble in organic solvents and also biferrocenyl by heating diferrocenylmercury with palladium black. Later Rausch[80] used silver in this reaction. Biferrocenyl was isolated as a byproduct of the interaction of a mixture of ferrocenyl-lithium and ferrocen-1,1′-ylenedilithium with tri-n-hexylbromosilane[81].

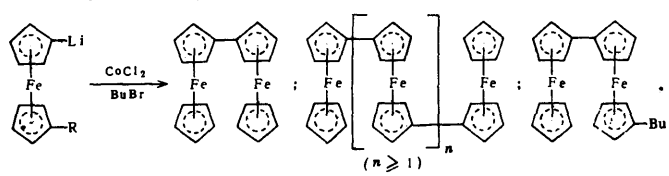
Nesmeyanov et al.[82] found that the action of an ammoniacal solution of silver oxide or of copper sulphate solution on ferrocenylboronic acid yields biferrocenyl together with ferrocene. According to Perevalova and Nesmeyanova[83] and also Rausch[80,84,85] halogenated ferrocenes undergo the Ullmann reaction with copper to give a high yield of biferrocenyl.

Rausch[80] and Nesmeyanov et al.[86] synthesised various derivatives of biferrocenyl. Reaction of a mixture of bromoferrocene and 1,1′-dibromoferrocene with copper at 105–120°C yielded biferrocenyl, 1,1′-terferrocenyl, and higher homologues[86], which were isolated by chromatography on aluminium oxide:



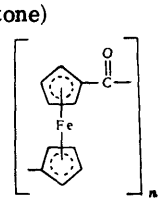
When only 1,1′-dibromoferrocene was used, 1,1′-terferrocenyl was formed in lower yield. The disubstituted terferrocenyl-1,1′-diferrocenyl-3,3′-diferrocenylferrocene was also obtained.

The preparation of a polyferrocenyl directly from ferrocenyl-lithium has been described[87,88]. The latter compound and cobalt chloride react, in the presence or in the absence of n-butyl bromide, to give various polyferrocenyls and butylated polyferrocenyls:

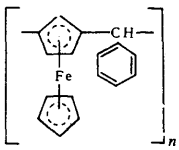


Many polyferrocenyls, butylated polyferrocenyls, and also biferrocenyl, terferrocenyl, and butylated biferrocenyl were isolated.

Pohl [? (Ed. of Translation)] reports the semiconductor properties of several ferrocene-containing polymers[89,90]. The poly(ferrocene ketone)

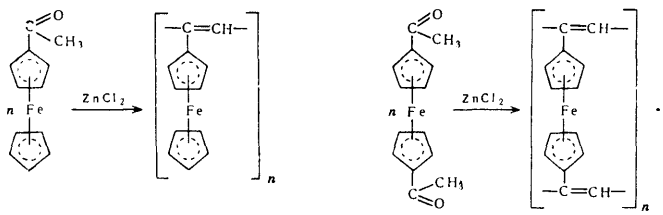


containing ferrocene molecules linked by carbonyl groups, has a conductivity of 10^{-13}–10^{-12} ohm^{-1} cm^{-1}†. The polymer having the highest conductivity is able to rectify a current in the presence of a silver–platinum couple. The polymer obtained by the condensation of ferrocene with benzylidene derivatives



exhibits a conductivity of 10^{-7}–10^{-8} ohm^{-1} cm^{-1}. Several of these polymers are thermoplastic materials.

Conjugated ferrocene-containing polymers possessing semiconductor properties were prepared by Paushkin, Vishnyakova, and their coworkers[31-33] by the polycondensation of acetyl- and 1,1′-diacetyl-ferrocene in the presence of zinc chloride in an autoclave at 200°C. Polyferrocenylvinylenes were obtained in good yields. The bulk of the polymers was insoluble and did not melt up to 500°C, while the benzene-soluble fraction melted at 260–270°C. The synthesis of the polyferrocenylvinylenes can be represented by the scheme



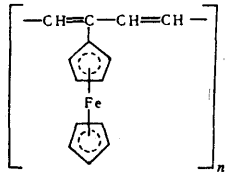
All these polymers exhibit signals in the e.s.r. spectrum and an exponential temperature dependence of the electrical conductivity, which is characteristic of semiconductors. An interesting temperature dependence is shown by the polymer obtained by the polycondensation of 1,1′-diacetylferrocene. Heating this specimen at 10^{-4} mm to 250°C leads to a sharp increase in its conductivity by a factor of 10^7, the activation energy being 1.5 eV. Subsequent heating and cooling of the specimen at 10^{-4} mm does not produce any appreciable change in its conductivity. The activation energy in such a process is 0.05 eV, which lies at the limit of accuracy of the measurements.

Polyferrocenylvinylenes, as well as several ferrocene-containing polymers obtained by polyrecombination, have been investigated by means of Mössbauer spectroscopy, which will make it possible to obtain information both on the electronic state of the iron atoms present in the polymers and on the general structure of the polymer[91].

A method has also been elaborated for synthesising polyferrocenylvinylenes from acetyl- and 1,1′-diacetylferrocene and calcium carbide[92]. The explanation is that the calcium carbide, while abstracting water from the acetylferrocene, is hydrolysed by it. The acetylene thus liberated may give polymers containing conjugated double bonds with the starting materials and with the initial products of the reaction.

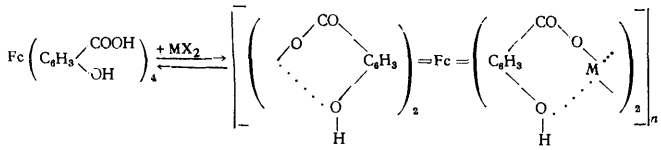
† The Russian original has 10^{-3}–10^{-12} Ω^{-1} cm^{-1} (Ed. of Translation).

The polymer is an infusible black powder, for which elementary analysis indicates the structure



Several papers have been published recently on the synthesis of polymeric chelate compounds and on their thermal stability and specific properties[93,94]. Until a few years ago, however, there was no information on polymeric chelates based on ferrocene or any other non-benzenoid aromatic compounds. Attempts to synthesise such polymers from the corresponding tetraketones of ferrocenes were in vain owing to intramolecular cyclisation[95]. Berlin and Kostroma[96] obtained polymeric chelate compounds of salicylic derivatives of ferrocene, using mainly ferrocenedisalicylic and ferrocenetetrasalicylic acids[95,97], which were treated with methyl acetylacetonates or with solutions of the corresponding salts.

Chelate compounds of ferrocenedisalicylic acid with silver and copper and polychelates of ferrocenetetrasalicylic acid with copper, magnesium, aluminium, beryllium, and tervalent iron were synthesised in yields[64] of 99%, these being almost black powders, insoluble in organic solvents and decomposed by water and alkalis. The tetrasalicylic acid, in contrast to the disalicylic acid, exhibits a strong tendency to polycondensation:



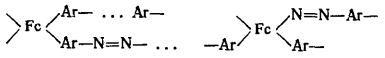
where Fc represents a ferrocene residue.

Examination of the thermal stability of the resulting polymeric chelate compounds of ferrocenetetrasalicylic acid at temperatures from 150° to 300°C showed that the beryllium complexes were the most stable, losing less than 5% of their weight when heated at 200°C for 5 h. The presence of conjugated bonds, ferrocene units, and metal atoms of variable valency in these polymeric chelates is responsible for their specific magnetic and electrical properties. Monomeric ferrocenedisalicylic and ferrocenetetrasalicylic acids are diamagnetic. When the temperature is raised (to 165°C) they acquire paramagnetic properties. The magnitude of the magnetic susceptibility of the polymeric chelate compounds is determined to a considerable extent by the nature of the metal forming part of the ring.

The electrical properties of polymers containing conjugated double bonds can be improved by including in the conjugated chain nitrogen atoms, the lone electrons of which participate in the π-electron system of the conjugated double bonds.

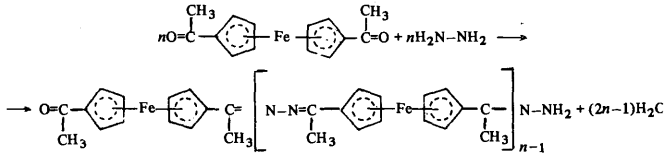
Berlin et al.[98] prepared ferrocene polymers containing nitrogen and a conjugated system by the interaction of ferrocene with biphenyl-4,4′-bisdiazonium and 3,3′-dicarboxybiphenyl-4,4′-bisdiazonium derivatives. From the elementary analysis, infrared spectra, solubility, and viscosity of the resulting polymers these workers considered that

the most probable structure had a parallel arrangement of the biphenyl or biphenyldicarboxylic acid residues:



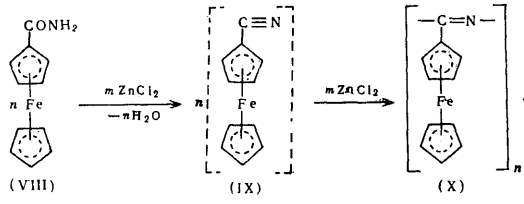
The fractions of the resulting polymers which were insoluble in organic solvents were infusible and thermostable in an inert atmosphere, losing ~ 8% of their weight at 700°C. On the admission of oxygen the polymers ceased to be thermostable. The polyazophenyleneferrocenes obtained give e.s.r. signals and possess static paramagnetism. Their electrical conductivity at room temperature is 10^{-16}–10^{-10} ohm^{-1} cm^{-1}.

The polycondensation of 1,1′-diacetylferrocene with hydrazine yields a ferrocene-containing polyazine, in which nitrogen atoms are linked together directly[99]:

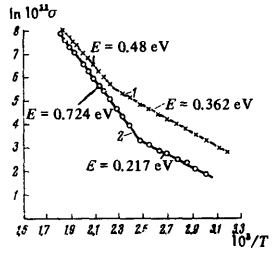


1,1′-Diacetylferrocene has been subjected to polycondensation also with diamines (*p*-phenylenediamine, benzidine, and hexamethylenediamine).[100] Conjugated ferrocene polymers containing nitrogen have been obtained by the polycondensation of ferrocene with hydroxylamine hydrochloride in the presence of zinc chloride[101].

Poly(ferrocenyl cyanide) has been obtained[102] by the polycondensation of ferrocenylformamide in the presence of zinc chloride. The first stage of the reaction involves the formation of ferrocenyl cyanide (IX), this being followed by complex formation and the ordering of its molecules with zinc chloride, and subsequent polymerisation at the C≡N bond leads to the formation of poly(ferrocenyl cyanide) (X):



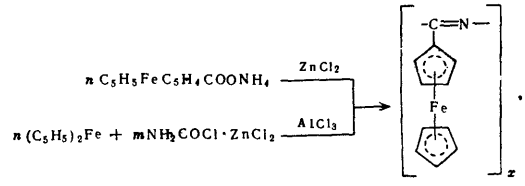
The reaction was carried out, with molar proportions of monomer : catalyst = 1 : 0.2–1, at temperatures of 80–170°C for 1½–5 h.



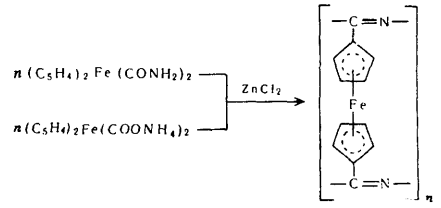
Temperature dependence of electrical conductivity of poly(ferrocenyl cyanide) after: 1) conditioning up to 50°C; 2) conditioning up to 50° and three conditionings up to 300°C.

All the insoluble products remain unmolten up to 500°C, are soluble in dimethylformamide, decompose over the range 420–500°C, and have a molecular weight of 1200. The poly(ferrocenyl cyanide) obtained gives an e.s.r. signal. The number of electrons having unpaired spins is 10^{18} g^{-1}. The temperature dependence of the electrical conductivity is exponential in character (see diagram).

Poly(ferrocenyl cyanide) has since been obtained by the polycondensation of ammonium ferrocenecarboxylate, and also directly from ferrocene and carbamoyl chloride (in the form of its zinc chloride complex)[103]. The infrared spectra and the elementary composition of the polymers were the same as for the poly(ferrocenyl cyanide) synthesised by the polycondensation of ferrocenylformamide. The reaction was conducted in an autoclave under various conditions.



The polycondensation of the diamide and of the diammonium salt of ferrocene-1,1′-dicarboxylic acid in the presence of zinc chloride yields poly(ferrocenylene dicyanide)[103,104]:

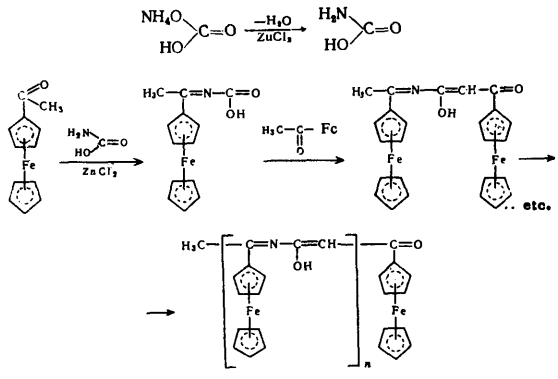


Poly(ferrocenyl cyanides) are dark coloured powders. The insoluble fractions do not melt up to 500°C, and the soluble fractions change colour at 350–500°C. The molecular weight of the soluble fractions determined isopiestically lies between 1200 and 1600. All the polymers give a narrow signal in the e.s.r. spectrum (10^{17}–10^{20} spins g^{-1}). The conductivity of the specimens is 10^{-14}–10^{-8} ohm^{-1} cm^{-1} at 50°C.

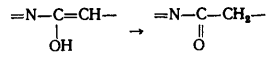
A ferrocene polymer containing nitrogen and a conjugated system has been obtained also by the polycondensation of acetylferrocene with urea in the presence of zinc chloride[105]. It give a single symmetrical signal in the e.s.r. spectrum having an integral intensity of 10^{18} spins g^{-1}, and its conductivity is 4.7×10^{-7} ohm^{-1} cm^{-1}.

An investigation has been made also of the polycondensation of acetylferrocene with ammonium hydrogen carbonate in the presence of zinc chloride, as a result of which novel ferrocene polymers have been obtained containing nitrogen, conjugated double bonds, and hydroxy-groups in the side-chains[106]. The reaction was conducted with various proportions of monomers and catalyst in an autoclave and at atmospheric pressure at 100–300°C for several hours. The yield of reaction products was 28–80% of theoretical.

The initial stage of the process probably involves conversion of the ammonium hydrogen carbonate into carbamic acid, which then reacts with the acetylferrocene:



It is possible also that the polymer chains may be cross-linked by means of the hydroxy-groups with the formation of ether links. The rearrangement



probably does not take place, since analyses show the presence of hydroxy-groups in the polymers.

Conjugated ferrocene polymers containing nitrogen have been obtained also by the polycondensation of ferrocenylformamide with acetaldehyde and butyraldehyde[107]. The reaction was conducted with various proportions of monomers and catalyst (zinc chloride) at 100–350°C for 3–10 h. The resulting polymers were paramagnetic. They give single symmetrical e.s.r. signals having a g-factor of ~ 2, a width of 2.7–5.4 oersteds, and an integral intensity of 10^{16}–10^{18} spins g^{-1}. The conductivity at 50°C is 10^{-10}–10^{-11} ohm^{-1} cm^{-1}.

TABLE 5. Electrical properties of conjugated ferrocene polymers obtained by polycondensation.

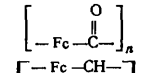
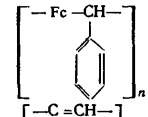
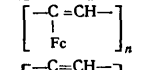
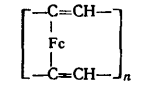
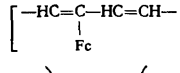
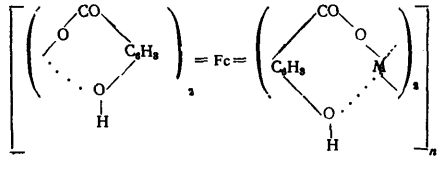
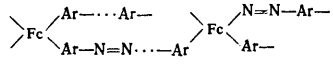
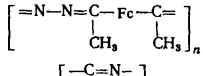
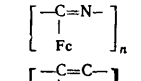
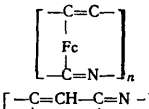
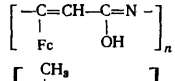
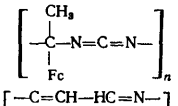
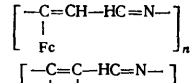
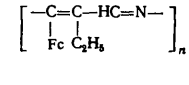
Structure of polymer	Concn. of unpaired electrons, g^{-1}	Conductivity σ_{50}, ohm^{-1} cm^{-1}	Activation energy ΔE, eV
	—	10^{-9}—10^{-12}	—
	—	10^{-7}—10^{-8}	—
	10^{17}	10^{-10}	1.45
	10^{17}	10^{-11}	0.42
	10^{16}	—	—
	signal in e.s.r. spectrum	10^{-8}—10^{-10}	—
	ditto	10^{-10}—10^{-10}	—
	10^{15}	—	1.48—2.78
	10^{17}—10^{19}	10^{-10}—10^{-12}	0.190—0.620
	10^{17}—10^{18}	10^{-11}—10^{-12}	0.115—0.630
	10^{17}	10^{-10}	0.05—0.350
	10^{20}	10^{-8}	0.070—0.455
	10^{18}	10^{-10}	0.047—0.271
	10^{18}	10^{-10}	0.158—0.230

Table 5 gives some electrical properties of the conjugated ferrocene polymers obtained by polycondensation.

5. FIELDS OF APPLICATION FOR POLYMERS CONTAINING FERROCENE

Polymers containing ferrocene are novel, as yet little studied macromolecular compounds. But the possibility of using these polymers for various purposes has already been demonstrated.

Several ferrocene-containing polymers exhibit the properties of electron-exchange resins[9-12], which can be used for the preparation of hydrogen peroxide, the removal of dissolved oxygen from water, the preparation of free iodine, the reduction of noble metals in solutions of their salts, etc.

Various silicon-containing polymers of ferrocene[75] can be used as the chief or secondary components of lubricants, hydraulic liquids, elastomers, plastics, and additives. It is possible also to formulate from them a series of compositions which can be employed as intermediates for the synthesis of resins, elastic materials, and organic metal carriers.

Ferrocene-containing polymers having conjugated double bonds, e.g. poly(ferrocene ketone)[89,90], possess the properties of organic semiconductors.

The possibility has been shown of using conjugated ferrocene polymers[102-107] as inhibitors of the degradation of rubbers by heat and oxidation and of the polymerisation of styrene[108]. Such polymers containing nitrogen are capable of forming complexes with salts of noble metals, which makes possible their use for extracting the latter from solutions.

Conjugated ferrocene polymers are catalysts of semiconductor type for the decomposition of alcohols and the synthesis of ammonia.

Several ferrocene polymers, e.g. products of the polycondensation of ferrocene with aldehydes and ketones[67], can be used as oxidation catalysts.

The diverse fields of application of ferrocene-containing polymers explain the ever increasing interest taken in these compounds, and make it certain that researches on these lines will lead to important practical results.

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THE SOLUBILITY OF AMINE SALTS IN SOLVENTS OF LOW POLARITY AND THE INFLUENCE OF DILUENTS ON THE EXTRACTION PROPERTIES OF AMINE SALTS

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I. INTRODUCTION

Amine salts have found extensive application for the extraction of acids and metal salts from aqueous solutions[1]. Since the amine salts are viscous substances and in some instances even solids, they are used, like many other extractants, as solutions in solvents of low polarity, immiscible with water. Being substances of polar structure, amine salts are in many cases relatively sparingly soluble in such diluents, and their extractive power is greatly influenced by several of the latter. Thus the selection of a suitable diluent for the amine salts, i.e. a diluent in which the amine salts are readily soluble and do not lose their extractive properties, is an important task, and the investigation of the regular features relating the structures and properties of the amine salts and the diluents to their mutual solubility and the extractive power of the solutions is of considerable practical importance.

The regular features of the solubility of amine salts in various diluents and the influence of the diluents on the extractive power of the dissolved salts are closely related to one another, since they are determined by the same factors. The most important of these factors is the ratio of the energies of interaction of the molecules of the extractant and the compound being extracted with one another and with the molecules of the diluent[2]. The ratio of the energies of these interactions also determines the state of the molecules of the salt in solution, and this determines to a considerable extent the extractive power and solubility of these salts[3,4]. A particularly marked influence on the extractive power and solubility of amine salts is shown by the specific solvation of the positively and negatively charged parts of their molecules: this solvation results from the formation of hydrogen bonds or donor–acceptor bonds with the solvent, and leads to binding of the extractant or to a marked change in its properties[5].

A large amount of experimental data has now been published on the solubilities of amine salts in various diluents and on the influence of diluents on the extractive properties of these salts. The aim of the present review is to systematise these data and to explain the observed regular features. Since the nature of these regularities and the approach to their explanation may depend on whether specific solvation of the molecules of the amine salt by the molecules of the diluent takes place, it is convenient to examine separately the phenomena taking place in systems with and without specific solvation. To explain the phenomena observed in systems without specific solvation, thermodynamic methods are chiefly used, since the mechanism of the relatively weak intermolecular interactions in these systems has as yet been comparatively little studied. For systems in which specific solvation is observed, the regular features of the solubility and the influence of the diluent on the extractive power of amine salts with various structures can be explained qualitatively on the basis of published information on the reactions of the diluent molecules with the molecules of the amine salts. The present review first gives data on the state of amine salts in solvents of low polarity, necessary for an understanding of the mechanism of these interactions.

II. THE STATE OF AMINE SALTS DISSOLVED IN SOLVENTS OF LOW POLARITY

Amine salts capable of extracting acids and metal salts are usually polar substances[5]. The dipole moments of their molecules[6] may reach 10–12 D. The factors determining the structures of these salts have been examined in detail[5,7-11].

In non-solvating solvents of low polarity, because of the low dielectric constant of the medium, dissolved amine salts are present almost completely in the undissociated state[8-16]. Moreover, the molecules of the salts in these solutions are usually appreciably associated (polymerised). It is appropriate in the present review to examine in detail data on the association of amine salts, since the degree of association of a dissolved substance is directly related to its solubility. When the size of the associated complexes of dissolved molecules reaches a definite limit, formation of a new phase takes place†. It is to be expected that all the factors facilitating a decrease in the association of an amine salt in solution should lead to an increase in its solubility.

The degree of association is determined by the ratio of the energies of interaction of the polar molecules (ion pairs) of the salt with one another and with the molecules of the solvent. It is evident that the interaction of the molecules of the salt with one another facilitates association, whereas interaction with the medium hinders it.

The interaction of the polar molecules or ion pairs of a solute with one another and with the medium is determined by a number of forces of different kinds[17-22]—electrostatic forces and dispersion forces—and an important part may also be played by weak donor–acceptor interactions,

† Voyutskii[3] points out that "... association complexes form the nuclei of a new phase in the old, so that here we have a striking example of a quantity-quality transition".

leading to the formation of charge-transfer complexes of low stability. In some instances hydrogen bonds or relatively strong donor–acceptor bonds are formed by the solute molecules with one another or with the solvent molecules. These main forms of interaction are characterised briefly below, and their influence on the association of molecules of amine salts having different structures in diluents of low polarity is examined.

The electrostatic interaction energy of the cation and the anion of the salt with the solvent is determined according to Born[23] by the relationship

$$A = \frac{Z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \quad (1)$$

(where Ze and r are the charge and the radius of the ion respectively, and D is the dielectric constant of the medium) and it follows that the electrostatic interaction energy of the ions with the medium decreases with decrease in the dielectric constant of the medium. In non-polar solvents or solvents of low polarity (saturated hydrocarbons, benzene, its alkyl derivatives, etc.), this energy is extremely low. The same is true of the dipole–dipole interaction energy between solute and solvent molecules. According to Keesom[24], the mean energy of attraction between dipoles is given by the formula

$$A = -\frac{2\mu_1^2\mu_2^2}{3r^6kT}, \quad (2)$$

where μ_1 and μ_2 are the dipole moments of the ion pairs or molecules, r is the distance between them, k Boltzmann's constant, and T the absolute temperature. It is evident that dipole–dipole interaction between the dipoles of a salt and the molecules of a non-polar solvent can take place only as a result of the production of induced dipoles in the molecules, and for non-polar solvents whose molecules are only slightly polarisable, this interaction should also be small. According to formula (2), the electrostatic interaction of the polar molecules of the salt with one another should be relatively large. This interaction is intensified with increase in the dipole moments of the molecules, with decrease in the distance between the dipoles (i.e. with decrease in the size of the salt molecules), and also with fall in the temperature.

Since in non-polar, non-solvating solvents the interaction of salt molecules with the medium is small, while their interaction with one another is considerable, appreciable association of the salts is observed in these systems. With increase in the polarity of the solvent we should expect an intensification of the electrostatic interaction of the molecules of the salt with the solvent and a decrease in the association.

The interaction of the molecules of amine salts with the molecules of non-polar organic solvents is determined to a considerable extent by dispersion forces, which increase with increase in the electronic polarisability of these molecules[25,26]. These forces oppose the association of the dissolved salts, but since they are relatively weak, they can bring about a significant decrease in association only when the electrostatic interaction of the salt molecules with one another is reduced as a result of marked screening of their charges by long hydrocarbon chains in the salt.

Charge-transfer complexes may be formed in the reactions of many compounds, including non-polar compounds[21,27-43]. In these complexes, one of the compounds acts as a Lewis acid and the other as a base. The stability constants of these complexes usually do not exceed a few units, and the interaction energy does not exceed 0.5–1 kcal mole^{-1}.[40] Nevertheless, these interactions can apparently have a marked influence on the state of certain salts in solution[44]. The ability of many aromatic hydrocarbons to form charge-transfer complexes has been reported[41,45-48]. In most instances the aromatic hydrocarbons in these complexes act as bases, but examples of their behaviour as Lewis acids have also been described[49,50]. The salts of primary and secondary amines in such complexes can in principle act as Lewis acids if the interaction takes place through the cation of the salt, or as bases if the interaction takes place through the anion of the salt. The salts of long-chain tertiary alkylamines, unlike the salts of secondary and primary amines, apparently cannot act as Lewis acids, since the positive charge of the cation in these compounds is strongly screened by the alkyl groups, and the compounds can act only as bases. The stability of charge-transfer complexes in which the aromatic diluent acts as a base increases with increase in its basic character, which can be assessed from data on the inductive effects of substituents in the benzene ring[25]. The formation of charge-transfer complexes between the molecules of amine salts and diluents would evidently oppose association in these systems. It should be noted, however, that the formation of charge-transfer complexes cannot always alter significantly the association of the amine salt, since the energy of bonding in these complexes is low.

The strongest interactions of the molecules of an amine salt with the molecules of a solvent and with one another are produced when hydrogen bonds are formed between these molecules. Hydrogen bonds may be formed between the anions of amine salts (which exhibit electron-donating properties[5]) and the molecules of the solvent if the latter contain electropositive hydrogen atoms‡. Hydrogen bonds may also be formed between the cations of amine salts, which contain electropositive hydrogen atoms, and the molecules of solvents which are electron donors§[14,15,52-60]. These bonds are so stable (energy 4–6 kcal mole^{-1}) that in many cases they have a decisive influence on the association of salts in solutions[61]. In systems with specific solvation of this type, the dissolved salts of tertiary amines are usually present in the monomeric state.

The most stable association complexes of salt molecules are produced when hydrogen bonds are formed between the anions of some molecules of the amine salt and the cations of other molecules of this salt. Such aggregates can obviously be formed chiefly in solutions of salts of primary amines, whose cations contain electropositive hydrogen atoms which are not screened by a large number of alkyl chains.

It follows from the foregoing that in non-solvating solvents of low polarity the interaction of the polar molecules of amine salts with one another, and hence their association, should increase with increase in the dipole moments of these molecules, and should decrease with increase in the dimensions of the latter and with increase in temperature. The association of the salts should decrease with increase in the polarity of the diluent and in its ability to form charge-transfer complexes or hydrogen bonds with the salt, and should increase when bonds of these types are

‡ Examples of these solvents are alcohols, acids, chloroform, etc.[21,25].

§ Examples of these solvents are ketones, ethers, esters, aromatic compounds containing mobile π-electrons, nitro-compounds, nitriles, etc.[21,25].

formed by the salt molecules with one another. Published data on the influence of some of these factors on the association of amine salts in solutions are given below.

1. Influence of the Polarity of the Molecules of Dissolved Amine Salts on Their Association in Solution

For a series of salts with similar structures, whose molecules have dipole moments of 0.29, 1.20, 1.66, and 2.67,[64-66] the degree of association in benzene solutions has the values 9, 12, 20, and 60 respectively[62,63]. The degree of association of amine salts also increases with increase in the polarity of their molecules[67-71]. Comparison of published data shows that in benzene solutions the degree of association of trioctylammonium salts varies in the sequence—perchlorate[72] > hydrogen sulphate[73-77] > nitrate[68,69] > sulphate[78]—in accordance with the order of their polarity. The association of tridodecylammonium halides in benzene, carbon tetrachloride, and cyclohexane varies in the order—iodide > bromide > chloride[79]—again in accordance with the change in polarity of these salts.

2. Influence of the Dimensions and Shape of the Molecules of Dissolved Amine Salts on Their State in Solution

Increase in the length of the alkyl chains in amines leads to a decrease in the association of their nitrates[6,52,68,80-87]. The degree of association of decyldimethylammonium, tri-n-octylammonium, tri-n-decylammonium, and tri-n-dodecylammonium nitrates at the same concentrations in *p*-xylene has the values ~ 12, 3–4, 2, and 2 respectively[68]. Tri-n-alkylammonium nitrates with hydrocarbon chains longer than C_{10} in solvents of the xylene and benzene type apparently do not form aggregates larger than the dimers[68,88,89]. The tendency of amine sulphates to undergo association also decreases with increase in the length of their alkyl chains[90].

The salts of some secondary amines are more extensively associated in solvents of low polarity than are the salts of the corresponding tertiary amines, formed with the same acids[91,92]. This can be attributed to the lower steric hindrance to the approach and mutual attraction of the dipole molecules for the salts of secondary amines compared with the salts of tertiary amines¶.

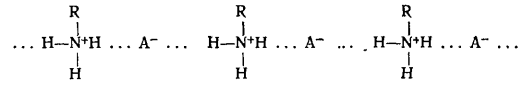
A decrease in the association of many salts containing organic radicals[62,63,93], including amine salts[9], is facilitated by the presence of double bonds in the hydrocarbon chains of their molecules, since the double bonds increase the rigidity of the chains and hence increase the steric hindrance to mutual approach of the salt molecules.

The degree of association of amine salts in non-polar solvents may depend on their concentration in the solutions[69,71], the nature of the dependence being different for salts with different structures[9]. The association of most salts of tertiary amines increases with increase in their concentration, passes through a maximum, and then decreases with further increase in the salt concentration[9,69]. For salts of tertiary amines with large anions the degree of association at moderate concentrations increases in conformity with the law of mass action[67,71,72,75,79,94]. For salts with relatively small anions[9], e.g. tri-n-octylammonium nitrate[95-97], tri-n-hexylammonium nitrate[98,99], tribenzylammonium halides[9], and various other salts having similar structures[100], the association increases with concentration more slowly than is required by the law of mass action†.

Highly associated salts are unique: their polymerisation is due to the formation of intermolecular hydrogen bonds. These salts are extensively associated at all concentrations.

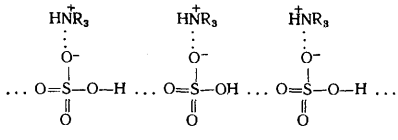
3. Influence of Intermolecular Hydrogen Bonding in Amine Salts on Their State in Solution

The formation of intermolecular hydrogen bonds is most characteristic of salts of primary amines, since the cations of these salts each contain three electropositive hydrogen atoms capable of taking part in the formation of these bonds[4,53-60,100-107]. On the other hand, the anions of amine salts may act as proton acceptors[5]. It is therefore suggested[5,51,68] that hydrogen bonds may be formed between cations and anions in different molecules of the salt of a primary amine, with the formation of relatively large and stable aggregates of the type



The salts of tertiary amines, particularly amines with long chains, cannot form such bonds because of steric hindrance and the smaller number of electropositive hydrogen atoms. With the salts of secondary amines, in view of the lower steric hindrance, the formation of intermolecular hydrogen bonds is more likely. Cryoscopic studies[68] show, however, that the nitrates of secondary amines are not associated much more extensively than are the nitrates of tertiary amines. The formation of intermolecular hydrogen bonds is apparently not characteristic of salts of secondary amines having long alkyl chains.

With the salts of secondary and tertiary amines intermolecular hydrogen bonding can be expected only when they are acid salts of dibasic or polybasic acids[76,108]. We can then assume the formation of aggregates of the type



in which the protons of the anions of some molecules of the salt interact with the electron-donating atoms of the anions of other molecules of the salt. It has in fact been shown that tri-n-octylammonium hydrogen sulphate[74-78,108] and hydrogen oxalate[109] are more extensively associated than are the corresponding normal salts of these acids. The more extensive association of the acid salts, however, may be due, not only to the formation of intermolecular hydrogen bonds between their molecules, but also to the higher polarity of these salts[78], resulting from the asymmetry of their structure.

It is to be expected that the association of amine salts may be influenced by the formation of hydrogen bonds between the anions of these salts and water molecules, when

¶ Another reason for the weaker association of salts of tertiary amines is the absence of intermolecular hydrogen bonds between the molecules of the salts of these amines.

† For the association of these salts the law of mass action is probably observed only at very low concentrations.

the latter are present in the system. Barrow and his coworkers[103] showed that the presence of water may lead to the dimerisation of amine salts with the formation of compounds of the type AmineHA... H–O–H... AHAmine, where HA is the acid forming the salt. Vdovenko and his coworkers[88] and also Högfeldt[104] had previously established that tri-n-octylammonium nitrate forms hydrates in the presence of water. Work by others[68,69], however, shows that the influence of water on the association of trialkylammonium nitrates is slight.

When hydrogen bonds are formed between the molecules of an amine salt, the association of the salt may be diminished significantly only as a result of specific solvation of the molecules of the salt by solvent molecules: non-solvating solvents have relatively little influence on the state of the salt in solution. If, however, the association of the amine salt takes place only as a result of dipole–dipole interactions, the nature and properties of a non-solvating solvent (dielectric constant, etc.) have a considerable influence.

4. Influence of the Dielectric Constant of the Medium on the State of Amine Salts in Solution

The influence of the properties of solvents on the association of the molecules of amine salts in solution has been investigated by a number of authors in studies of the electrical conductivities of these salts[8,9,80–86,100–112], and also in studies of the extraction of acids and metal salts by amine salts[68,69,73–77,79,87,98,113–116]. Sukhotin[8] and Kraus and his coworkers[6,9,80–86] have shown that the salts of tertiary amines and quaternary ammonium bases, which are present in the monomeric state in polar solvents (e.g. nitrobenzene), are associated in benzene and other non-polar solvents. Fomin and his coworkers[69,74], Shmidt and Shesterikov[68], Frolov and Sergievskii[77], Vdovenko, Chaikhorskii, and their coworkers[88,98], and others[70,79,87,113,115,116] have studied the state of the salts of various tertiary alkylamines in *p*-xylene, benzene, and toluene, and have shown that the amine salts are appreciably associated in these solvents of low polarity. The increase in the degree of association observed with decrease in the dielectric constant of the medium is consistent with the decrease in the strength of electrostatic interaction of the salt molecules with the medium, following from formulae (1) and (2).

5. Association of Salt Molecules in Various Non-Polar Solvents

The dielectric constant is not the only property of a solvent determining the association of a salt dissolved in that solvent. For example, the association of trialkylammonium nitrates in octane[113] is much greater than the association of these salts in benzene and *p*-xylene[68], although the dielectric constants of all these solvents are similar and the dipole moments of their molecules are zero[117]. According to Palit's data[118], the degree of association in benzene and in cyclohexane has the values ~ 5 and ~ 10 respectively for dodecylammonium propionate, and ~ 3 and 10 respectively for dodecylammonium oleate, although the molecules of both these solvents are non-polar. The degrees of association of tridodecylammonium halides are also different for these solvents of equal polarity[79].

These differences in the degree of association of salts in different non-polar solvents are due to differences in the strength of the non-Coulombic interactions (dispersion interactions, etc.) of these non-polar solvents with the dissolved amine salts, and also, apparently, to the formation of unstable charge-transfer complexes between the amine salts and certain solvents. For a rough estimate of the influence of these interactions on association, we can use the values of the Hildebrand parameter δ, characterising the strength of the interaction of the molecules of each component of the solution with one another[2,19,45,119,120]. The greater the difference in the force fields of the molecules of the various components of the solution, i.e. the greater the difference between the parameters δ characterising these components, the greater should be the tendency for identical molecules to associate‡. The values of δ for amine salts are usually much greater than those for most non-polar diluents, and amount to 10–14 $cal^{1/2}\ cm^{-3/2}$.[121,122] For solvents of low polarity, the values of δ lie in the range 7–9 $cal^{1/2}\ cm^{-3/2}$ (see Table). The difference in the values of δ for the salt and the solvent increases on going from aromatic to aliphatic hydrocarbons (see Table), in agreement with published data on the association of amine salts in these solvents. The Table also shows that the value of δ for cyclohexane is lower than that for benzene. This agrees with the observed more extensive association of mono- and tri-dodecylammonium salts in cyclohexane compared with benzene[118]. Published data[123] indicate that the degree of association of trioctylammonium chloride is greater in cyclohexane than in toluene, and this again agrees with the higher value of δ for toluene. The degree of association of these salts has its highest values in open-chain saturated hydrocarbons, whose δ-values are much less than those for cyclic hydrocarbons and differ to the greatest extent from the values of δ for amine salts[113]. Amine salts are less associated in carbon tetrachloride than in cyclohexane[79], since the former solvent has the higher value of δ. The data in the Table also suggest that the association of salts dissolved in alicyclic hydrocarbons should decrease on going from cyclopentane to cyclo-octane.

The force of interaction between the molecules of different substances in solution depends also on their molar volumes[45]. Thus within a given class of solvents, satisfactory correspondence between the values of δ and the degree of association of salts is observed only when solvents having similar molar volumes are compared.

6. Association of Salts and Their Solubility

On the basis of the above data on the influence of the properties of salts and solvents on association, it is possible to reach preliminary conclusions regarding the influence of these properties on the solubility of amine salts in non-polar diluents and those of low polarity. Since diminished association of a salt leads to an increase in its solubility, it may be expected that the solubility of amine salts should increase with decrease in the dipole moments of their molecules, with increase in the number and length of the alkyl chains in the molecules, with the introduction of double bonds into the alkyl chains, with increase in the dielectric constant of the solvent, and (for non-solvating non-polar solvents having similar molar volumes) with increase in the parameters δ for these solvents, as well as

‡ This argument will obviously be completely valid only in the absence of specific interactions between solvent and solute.

TABLE. Parameters δ for various solvents[19,45,119,124-126].

Class of compound	Solvent	δ	Class of compound	Solvent	δ
Saturated open-chain hydrocarbons	Neopentane	6.2	Aromatic hydrocarbons	n-Butylbenzene	8.6
	Isopentane	6.8		n-Propylbenzene	8.6
	n-Pentane	7.1		Ethylbenzene	8.8
	n-Hexane	7.3		Toluene	8.9
	n-Heptane	7.4		Benzene	9.2
	n-Octane	7.5		o-Xylene	9.0
	n-Nonane	7.6		m-Xylene	8.8
	n-Decane	7.7		p-Xylene	8.8
	n-Dodecane	7.8		Mesitylene	8.8
	n-Tetradecane	7.9		Styrene	9.3
	n-Hexadecane	8.0		Naphthalene	9.9
	2,2,4-Trimethylpentane	6.8		Nitrobenzene	10.0
	Isopentane [sic]	6.6	Halogenated hydrocarbons	Bromobenzene	10.0
		7.3		o-Dichlorobenzene	11.0
		7.6		Chlorobenzene	9.5
Unsaturated hydrocarbons	Hex-1-ene	7.7		CCl_4	8.6
	Oct-1-ene			$CHCl_3$	9.3
	Hexa-1,5-diene	8.2		$CHBr_3$	10.5
				CH_2Cl-CH_2Cl	9.0
Saturated cyclic hydrocarbons	Cyclopentane	8.5		CH_2Br-CH_2Br	9.6
	Cyclohexane	8.6			
	Cycloheptane	7.8	Other compounds	Nitromethane	12.6
	Cyclo-octane			Carbon disulphide	10.0
	Methylcyclohexane			Dioxan	10.0
				Pyridine	10.7
				Acetonitrile	11.9
				Methyl ether	8.8

with rise in temperature. The formation of intermolecular hydrogen bonds or donor–acceptor and charge-transfer complexes between the molecules of the amine salt should decrease its solubility (as a result of which the salts of primary amines and the acid salts of polybasic acids have a low solubility), whereas the formation of corresponding bonds with the diluents should increase the solubility. The published regular features of solubility show good agreement with these conclusions.

III. THE INFLUENCE OF THE STRUCTURES AND PROPERTIES OF AMINES AND DILUENTS ON THE SOLUBILITY OF AMINE SALTS IN SYSTEMS WITHOUT SPECIFIC SOLVATION

Many of the conclusions regarding the regular features of the solubility of amine salts in diluents of low polarity, reached above from an examination of the state of these salts in solutions, can be reached also by thermodynamic methods. In some instances it is possible to predict the solubility quantitatively.

From the thermodynamic viewpoint, solubility may be determined by factors of two different types—(1) factors independent of the nature of the solvent and determined entirely by the nature of the solute, and (2) factors depending on the properties not only of the solute but also of the solvent.

For systems obeying the laws governing ideal solutions, the solubility of solids is independent of the nature of the liquid solvent. Liquids in ideal systems are miscible in all proportions.

For many real systems, the mutual solubility of liquids is restricted, and the solubility of solids in the liquids depends not only on their properties but also on the nature of the solvent. When real systems obey the laws of regular solution[19], the solubility values can be calculated from the parameters δ of solute and solvent. For solutions whose behaviour differs from that predicted by the theory of regular solutions, quantitative prediction of the solubility is difficult. Large changes in solubility on passing from one system to another, however, can be predicted qualitatively on the basis of this theory with allowance for the deviations expected on the basis of data on specific interactions in these systems. It is therefore of interest to examine the correspondence between solubility data for amine salts and the regular features expected for ideal and regular solutions.

1. Solubility in Ideal Systems

In ideal systems the solubility of solids is given by Shreder's equation[127,128]

$$\ln N = -\frac{\Delta H_f\,(T_f - T)}{RT_f\,T} \qquad (3)$$

where N is the mole fraction of the solute in a saturated solution, ΔH_f the heat of fusion of the solute, T_f the melting point of the solute, and T the temperature of the system.

It follows from Eqn. (3) that the solubility of solids in ideal liquid systems decreases with increase in the melting point and the heat of fusion, and increases with rise in the temperature of the system. This equation also shows that at the melting point the solubility is unlimited: i.e. ideal liquids are miscible in all proportions. The experimental data show good agreement with Shreder's equation for solutions of various non-polar substances in non-polar diluents[129]. It is evident that even qualitative conclusions regarding the solubility of amine salts in diluents of low polarity can be reached from Eqn. (3) only for amines of high molecular weight containing very large organic radicals, which screen the dipole moments of the salts, so that their behaviour and properties approach those of non-polar hydrocarbons.

The salts of tertiary amines with sufficiently high molecular weights are solids, and their melting points increase with increase in molecular weight. The salts of amines with very long hydrocarbon chains are sparingly soluble even in relatively polar solvents, in agreement with conclusions reached from Eqn. (3). From this it follows that the increase in the solubility of amine salts in non-polar solvents with increase in the length of the hydrocarbon chains of the amines, expected from considerations related to association of the salts, should be observed only within definite limits. The salts of amines with extremely long alkyl chains are sparingly soluble because of the increase in their melting point.

2. Solubility in Systems Obeying the Laws Governing Regular Solutions

Regular solutions are those in which the distribution of the components is completely homogeneous and disordered, the force fields of the molecules are symmetrical, and the molecular volumes of the molecules do not differ greatly from one another[19]. Solutions of non-polar substances in non-polar solvents correspond most closely to this definition and show the closest agreement with the rules derived for regular solutions[45,119,120]. For regular solutions the solubility differs from the ideal solubility, but quantitative allowance can be made for this deviation by means of equations containing the parameters δ. The solubility of solids

in regular solutions is determined[45] by the equation

$$\ln a^{i}_{\text{solid}} = \ln \varphi_2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right) + \frac{V_2\varphi_1^2(\delta_2 - \delta_1)^2}{RT}, \quad (4)$$

where a^{i}_{solid} is the ideal solubility, calculated from Eqn. (3), φ_1 and φ_2 are the volume fractions of solvent and solute in the saturated solution, V_1 and V_2 the molar volumes of these substances, and δ_1 and δ_2 their solubility parameters.

It follows from Eqn. (4) that, other conditions being equal, the solubility should be greater, the smaller the difference $\delta_2 - \delta_1$. Hildebrand[130-132] points out that Eqn. (4) is approximate and that caution must be exercised in using this equation to calculate the solubilities of polar substances[19], despite the fact that values of δ for a large number of polar substances have been published[133]. Although amine salts are polar substances, the principles of the theory of regular solutions are observed for many polar substances containing a bulky hydrocarbon portion, with an accuracy which is greater, the greater the volume of the non-polar radicals in the molecules of these substances[134]. The first attempt to apply the theory of regular solutions to the determination of the solubility of amine salts in non-polar solvents was made by Kertes[121,122], who determined the values of δ for a number of tertiary, secondary, and primary alkylammonium chlorides from their solubilities in various solvents. Similar values of δ were obtained for each salt in different solvents, indicating that the characteristic features of regular solutions are observed (approximately at least) with solutions of long-chain alkylamines. For primary, secondary, and tertiary alkylammonium chlorides the values of δ[121,122] are ~ 13–14, ~ 11–12, and 10.5–10.6 respectively, in agreement with the higher solubility of tertiary amine salts in solvents of low polarity. In accordance with Eqn. (4) and the values of δ given in the Table, the solubility of amine salts in saturated hydrocarbons is much less than that in aromatic hydrocarbons or in carbon tetrachloride. It may be expected that the regular features of solubility in non-solvating solvents will be analogous for other amine salts.

With solvents whose molar volumes have similar values, the solubility of amine salts should increase with increase in the value of δ for the solvent. The data in the Table indicate that for aromatic hydrocarbons the order of solvent power will be—nitrobenzene > chlorobenzene > benzene > toluene > xylene ≃ ethylbenzene > n-propylbenzene —which corresponds to the observed solvent power of these solvents for amine salts[135]. The observed sequence indicates that the solvent power of the diluent decreases with increase in the number and length of the alkyl substituents in benzene. An interesting parallelism is observed between the increase in the acidic properties (increase in ionisation potential[136]) of substituted benzene derivatives and their solvent power for the salts of tertiary amines. In this series of compounds the solvent power decreases with decrease in the acidic properties. If this regular feature is observed for other benzene derivatives, we may expect that all derivatives with substituents having positive inductive effects will be weaker solvents than derivatives containing substituents with negative inductive effects[137,138]. These results can be explained if we assume that the solubility of amine salts increases with increase in the acid–base interaction of the anions of the amine salts with the solvent molecules.

The data in the Table suggest that cyclohexane is a more effective solvent than open-chain hydrocarbons, but is less effective than aromatic hydrocarbons. The solubility of tri-n-octylammonium chloride in cyclohexane is in fact less than that in toluene, but much greater than that in saturated hydrocarbons[123]. In the selection of aromatic hydrocarbons for the dissolution of amine salts, compounds with a large number of long alkyl chains attached to the benzene ring should evidently be avoided as far as possible. The data in the Table show good agreement with the familiar ready solubility of amine salts in nitromethane, chloroform, and pyridine[139]. The data also suggest that the presence of naphthalene in benzene or carbon tetrachloride may increase their solvent power, and also that the solvent power of alicyclic hydrocarbons should vary in the order—cyclo-octane > cycloheptane > cyclohexane > cyclopentane > methylcyclohexane.

In the theory of regular solutions, the solubility of a liquid is determined by the relationship[19,5,119]

$$\ln N_2 = -\frac{V_2\varphi_1^2}{RT}(\delta_2 - \delta_1)^2, \quad (5)$$

where the subscripts 2 and 1 denote quantities relating to solute and solvent respectively§. Thus for liquids also, the solubility is determined by the difference $\delta_2 - \delta_1$, and we should expect the regular features of the solubility of liquid amine salts to be analogous to those observed for the solid salts.

For a preliminary estimate of the possibility of dissolving amine salts in solvents which do not exhibit specific solvation, an equation derived from the theory of regular solutions[45], relating the consolute temperature of a mixture of liquids with the parameters δ, is of interest:

$$T_{\text{cons}} = (\delta_1 - \delta_2)^2(V_1 + V_2)/4R \quad (6)$$

where V_1 and V_2 are the molar volumes of the components of the mixture. This equation and the value of δ for the amine salt can be used to determine approximately the solvents in which the salt will be soluble at ordinary temperatures. By substituting in Eqn. (6) the values of δ for amine salts determined by Kertes[121,122] and the known values of δ for various solvents, it can readily be established that for solutions of these salts in aromatic and chlorinated hydrocarbons the values of T_{cons} lie considerably below room temperature, whereas those for solutions in aliphatic hydrocarbons are much higher than room temperature, in agreement with the solubility data.

Thus the conclusions reached on the basis of the theory of solubility for regular solutions agree with the observed regular features of the solubility of amine salts, and the formulae of this theory, together with known values of δ, can be used to predict semi-quantitatively the solubility of the salts in various solvents.

All saturated hydrocarbons are poor solvents for amine salts. At the same time there are significant differences in the solvent power of individual saturated hydrocarbons. Thus the volume solubility of amine salts and various other polar organic compounds in hydrocarbons decreases with increase in the length of the hydrocarbon chain[121,122,140-142]. For example, the solubility of tridodecylammonium nitrate in octane is greater than that in decane[143]. At the same time, the values of δ for hydrocarbons increase slightly with increase in the chain length. Similar regular features

§ This equation is applicable when $V_2 \simeq V_1$. More complex equations are used when the difference between these volumes is large[45].

were observed in a study of the solubility of water in saturated hydrocarbons[144]. The solubility of water, expressed in mole fractions, increases slightly with increase in the length of the alkyl chains, the increase corresponding exactly to that expected from formula (5). On passing to long-chain hydrocarbons, however, the increase in molar volumes takes place so rapidly that the volume solubility of water in these hydrocarbons decreases, whereas the solubility expressed in mole fractions increases.

Thus in those instances where the values of δ change only slightly on going from one substance to another, the solubility (in volume fractions) is influenced chiefly by the change in the molar volumes, the volume solubility of the solute decreasing with increase in the molar volume of the solvent. This conclusion also agrees with the solubility rule derived by Semenchenko[145-147], according to which the mutual solubility of two substances increases with decrease in the difference in their "generalised moments" given by the ratios of the dipole moments of the molecules to their molar volumes. Since the polarity of the molecules of the amine salts is much greater than the polarity of the diluent molecules, the generalised moments of the amine salts are also greater than the generalised moments of the diluents. Thus the solubility of the salts in the diluents should increase with increase in the generalised moment of the diluent and with decrease in the generalised moment of the amine salt. When the dipole moments change little from one compound to another, the solubility should evidently be influenced chiefly by the values of the molar volumes. The solubility of a salt should increase with increase in its molar volume (since this leads to a decrease in its generalised moment) and with decrease in the molar volume of the solvent. The observed regular features of the solubility of amine salts in various solvents agree with these conclusions from Semenchenko's rule. For example, the solubilities of trialkylammonium nitrates in non-polar solvents change in the order—tridodecylamine > tridecylamine > trioctylamine[143]—and the solubilities of the sulphates change in the order—tertiary amine > secondary amine > primary amine[108,114,135].

These data also indicate that the solubility of salts of aromatic amines and amines with cyclic radicals should be less than the solubility of the salts of n-alkylamines containing the same number of carbon atoms, since the molar volumes of arylamines and cycloalkylamines are less than the molar volumes of the corresponding n-alkylamines.

Thus either Semenchenko's rule or the equations of the theory of regular solutions can be used to predict semi-quantitatively the solubility of various amine salts in diluents with different structures. The possibility of applying the theory of regular solutions for this purpose will probably increase with increase in the availability of data on the values of δ for various amine salts and diluents.

As already noted, these criteria are not valid when strong specific interaction takes place between the components of the solutions. Thus in a number of instances chloroform is a more powerful solvent than benzene, despite the fact that the value of δ for chloroform differs little from that for benzene. These deviations are due to the fact that specific solvation, which has a marked influence on solubility, takes place in amine salt–chloroform systems.

IV. THE INFLUENCE OF SPECIFIC SOLVATION ON THE SOLUBILITY OF AMINE SALTS IN DILUENTS OF LOW POLARITY

Amine salts dissolve readily in solvents which solvate their cations or anions as a result of the formation of hydrogen bonds. Thus acidic substances, capable of hydrogen bonding with the anions of amine salts[5,86,95,96,148-155] (organic acids and alcohols, and various chlorinated hydrocarbons), and also basic substances, capable of hydrogen bonding with the cations of amine salts[5,97,148,156] (ethers, ketones, nitro-compounds, and various amines), are usually effective solvents for amine salts and are miscible with them in all proportions. These substances prevent the association of amine salts by forming compounds with them, bringing them into solution¶. Basic diluents are more effective solvents for the salts of primary and secondary amines than for the salts of tertiary amines, since, as noted above, the formation of hydrogen bonds with these substances is least characteristic of the cations of the salts of tertiary amines. Acidic diluents dissolve the salts of tertiary amines more effectively than the salts of primary amines.

Substances which solvate amine salts are capable of dissolving these salts even when they are not used in the pure form; the addition of small quantities of many of these substances to amine salts increases considerably the solubility of the latter in non-solvating solvents of low polarity, e.g. in saturated aliphatic hydrocarbons[95,135,157-164]. The marked influence of various substances, added as a third component, on the mutual solubility of liquids and the solubility of solids in liquids was described at an early date. The action of a third component which increases solubility, known as solubilisation, was noted by Alekseev as early as 1879.[165] Timmermans[166] established that a third substance is able to increase the mutual solubility of two other substances if it is soluble in both of them. It is evident that an increase in the solubility of amine salts in non-solvating diluents may be achieved by the addition of substances which are capable not only of solvating the amine salts but also of dissolving in the diluents, i.e. substances of the types indicated above, whose molecules contain large hydrocarbon portions.

Several theories have been put forward to explain the mechanism and the regular features of solubilisation[167-169]. The most widespread are McBain's colloidal–adsorption theory[167], according to which the substance being dissolved passes into solution by being sorbed inside colloidal particles of the added solubilising agent, distributed in the solvent; and Winsor's solvation theory[168,169], which attributes the action of the solubilising agent to its simultaneous interaction with the substances in both the phases exhibiting negligible or limited miscibility. Experimental data obtained in recent years on the solubility of water in non-polar organic solvents[118,170,171] show more complete agreement with Winsor's theory than with McBain's theory. Apart from this, the colloidal–adsorption theory cannot be used to explain the regular features of the solubilisation of amine salts, since the solubilising agents added (alcohols,

¶ An example of the complete absence of association as a result of solvation of the anions of a salt by diluent molecules is provided by solutions of tridodecylammonium halides in chloroform[79]. In benzene these salts are appreciably associated.

ketones, and nitro-compounds) are not present in the organic solvents in colloidal form. Examination of the experimental data on the solubility of amine salts in solvents of low polarity in the presence of solubilising additives shows that these data can also be explained on the basis of the concepts of solvation theory.

1. The Use of Solvation Theory to Explain the Phenomena of the Solubilisation of Amine Salts

According to Winsor's theory[168,169], the efficiency of a solubilising agent depends on the value of the "affinity ratio" $R = A_{co}/A_{cw}$, where A_{co} measures the affinity of the solubilising agent for the phase of low polarity, and A_{cw} the affinity of the solubilising agent for the more polar phase. According to Winsor, the maximum increase in solubility per mole of solubilising agent added is reached when R is close to unity, i.e. when the affinities of the added third component for the two phases are the same. If two liquids—one polar and one non-polar—are immiscible and the value of R for an added third substance is greater than unity, this substance, when added to the system, enters the non-polar phase to a greater extent, and preferential dissolution of the polar substance in the non-polar phase takes place. When $R < 1$, the addition of the solubilising agent is accompanied by dissolution of the material of the non-polar phase in the polar phase. The quantity of solubilising agent required to homogenise the system when $R < 1$ and when $R > 1$ is greater than the quantity required when $R = 1$.

These qualitative ideas make it possible to predict the nature and the strength of the solubilising action of various additives on the solubility of amine salts in solvents of low polarity, in particular the action of alcohols having various structures.

The mechanism of the solubilising action of alcohols can be explained as follows. Alcohols are capable of solvating the anions of trialkylammonium nitrates, sulphates, chlorides, and iodides[95,96,172-175] with the formation of the relatively stable solvates $AmineHNO_3.2ROH$,[96] $[AmineH]_2SO_4.2ROH$,[172,173] $AmineHCl.ROH$,[61,174,175] and $AmineHI.ROH$.[176] This solvation leads on the one hand to breakdown of the salt aggregates to monomers[177] and on the other hand to dissolution of the salt in the solvent of low polarity, since the attachment of the alcohol molecules to the amine salt molecule leads to a decrease in the overall dipole moment of the resulting solvate and a simultaneous increase in its dimensions, including the dimensions of its hydrocarbon portion†. The number of alcohol molecules required for the solubilisation of low concentrations of tri-n-octylammonium nitrate in a non-polar diluent has recently been determined[178], and found to be 2 moles mole^{-1}, which agrees with the value of the solvate number found by other workers[96], who have studied the amine nitrate–alcohol system by physicochemical analysis. It also follows[178] that the dissolution of the amine nitrate in a non-polar solvent requires the formation of its solvate with the alcohol. The solvates formed by alcohols with amine salts are relatively stable. According to published data[96], the stability constants of the compounds $AmineHNO_3.2ROH$ for alcohols containing 6–12 carbon atoms in the chain are $\sim 10^3$ and differ little from one another, although the values decrease slightly with increase in the length of the alkyl chain of the alcohol. Since the interaction of alcohols with solvents of low polarity, e.g. saturated hydrocarbons, which is due entirely to van der Waals forces, is much weaker than with amine salts, the values of R in alcohol–amine salt–non-polar diluent systems are apparently much less than unity. Thus in a homologous series of alcohols a stronger solubilising action should be shown by alcohols characterised by a higher value of R, i.e. by alcohols with a higher affinity for the non-polar phase. We may thus expect that the solubilising action of aliphatic alcohols in amine salt–non-polar solvent systems will increase with increase in the length of the alkyl chains of the alcohols. This dependence of the solubilising power of alcohols on their structure was observed by Izmailov and Franke[171] and by Purnell and Bowden[179] for systems in which the bonding of the alcohol with the main material of the polar phase was much greater than that with the material of the non-polar phase.

With change in the properties of the amine salt, however, another type of relationship is possible. If the electron-donating power of the anion of the amine salt is low or if there is steric hindrance to the solvation of the anion by the alcohol, and if as a consequence the affinity of the alcohol for the salt is so low that it is less than its affinity for the non-polar solvent and $R > 1$, an increase in the solubilising action of the alcohol will be brought about by changes in its structure which lead to a decrease in R, i.e. to an intensification of its interaction with the amine salt and a decrease in the interaction with the non-polar diluent. This will evidently be observed with decrease in the length of the alkyl chain of the alcohol, since this intensifies the interaction of the alcohol with the amine salt[96]. These regular features are probably characteristic of the solubilisation of salts having bulky anions, whose electron-donating properties are weakened considerably, for example the salts of organic acids or the compounds of various metal salts, extractable by amines. The electron-donating properties of the anions of these salts may be very weak, so that their solvation by alcohols is very weak[179].

A solubilising action with respect to amine salts in non-polar solvents may evidently be shown not only by alcohols but also by other organic compounds which are capable of solvating these salts and are readily soluble in non-polar solvents. As noted above, this ability may probably be shown not only by alcohols but also by aliphatic acids with sufficiently long alkyl chains, phenol and its derivatives soluble in non-polar diluents, and other organic compounds with a large hydrocarbon portion which are electron acceptors, i.e. which have at least weak acidic properties and hence are capable of solvating the anions of amine salts. On the basis of Winsor's theory, it may be expected that, of the solubilising agents which are readily soluble in non-polar solvents, the most effective for the solubilisation of salts whose anions exhibit significant electron-donating properties, e.g. amine nitrates and chlorides, should be substances with weaker acidic properties than alcohols. These substances may be very weak aprotic acids, interacting with the anions of amine salts by a donor–acceptor mechanism. If, however, the acidic properties of these solvents, added as solubilising agents, are so weak that $R > 1$ and the strength of the donor–acceptor interaction of these substances with anions is comparable with that of the dispersion interactions with the non-polar solvent, Winsor's theory indicates that increase in the acidic properties of the solubilising agent should lead to an increase in solubility in the system. In this connection it is of interest to

† These changes lead to a decrease in the generalised moment[145-147] of the salt.

recall that the solvent power of aromatic hydrocarbons increases with increase in their acidic properties. The existence of this relationship indicates the possibility that these "non-solvating" diluents of low polarity dissolve amine salts as a result of weak donor–acceptor interactions with the anions of these salts.

Solubilisation can apparently take place as a result of solvation not only of the anions but also of the cations of amine salts. The solvation of cations may be of greatest importance for the solubilisation of the salts of primary amines[68] and the acid salts of dibasic and polybasic acids with any anions: it prevents the polymerisation of these salts which takes place as a result of the formation of hydrogen bonds between the cations of some molecules of the salt and the anions of other molecules of the salt[51]. The solubilising influence of the solvation of cations is less with secondary and tertiary amines, since less extensive solvation takes place than with primary amines, because of the greater steric hindrance and the smaller number of acidic hydrogen atoms in these amines[97]. The ability to solvate the cations of the salts of primary amines and to solubilise these salts is shown by substances which are electron donors[180,181]—ketones, ethers, esters, amides of carboxylic acids, nitro-compounds, etc.—and the ability (albeit weak) to solubilise the salts of primary amines is also shown by various substances which have very weak basic properties, e.g. benzene.

An interesting conclusion from Winsor's ideas is the possibility of the non-additive ("synergic") solubilising action of various agents. Studies of solubilisation in water–non-polar solvent systems[118,170] established that mixtures of solubilising agents, for one of which $R < 1$ while for the other $R > 1$, have a much greater solubilising action than each agent taken separately at the same concentration. Winsor attributes this to the fact that for this synergic mixture the value of R becomes close to unity. A very marked increase in solubilising power is observed at definite ratios of these solubilising agents, corresponding to $R = 1$.[118,171] It may be expected that, with solubilisation in amine salt–non-polar solvent systems, it is also possible to select solubilising agents, one mole of a mixture of which would give a greater (synergic) solubilising effect than would one mole of either component taken separately.

2. Solubilisation of the Extractable Compound by Excess of the Extractant

Various amine salts having a bulky inorganic complex anion do not dissolve even in relatively polar solvents, in which other salts of these amines, containing smaller anions, are readily soluble[158]. In these instances the solubility of the sparingly soluble amine salt can be increased as a result of its solvation by the molecules of a more soluble salt of the amine, present in solution. The salt $[R_3NH]_2[CoCl_4]$ in *p*-xylene is solvated by molecules of the extractant R_3NHCl.[182] Solvation of extractable amine salts by an excess of the extractant is also indicated by the fact that, in order to prevent separation into layers in organic solutions of low polarity, containing salts formed during extraction such as $[AmineH]_2[Pu(NO_3)_6]$ or $[AmineH].[UO_2(NO_3)_3]$, the presence of an excess of the simple salt $AmineHNO_3$ in the solution is required[158,183]. The dissolution of the salt $[AmineH]_4[U(SO_4)_4]$ in butylbenzene[184] also requires the presence, in the solvent, of the simple salt $[AmineH]_2SO_4$ in quantities sufficient for formation of the solvate $\{[AmineH]_2SO_4\}\{[AmineH]_4[U(SO_4)_4]\}$. Smulek and Siekierski[185], in a study of the dependence of the activity coefficients of the dissolved iron(III)–$[AmineH][FeCl_4]$ complex on the concentration of the extractant (AmineHCl), established that these coefficients decrease with increase in the extractant concentration. This phenomenon also can be attributed to a decrease in the concentration of free $[AmineH][FeCl_4]$ as a result of its solvation by AmineHCl molecules. The solvation of extractable complexes by molecules of amine salts used as extractants is also indicated by published data[186–188]. As in the solubilisation of amine salts by the addition of alcohols, the efficiency of the solubilising action of the amine salt used as extractant is greater the greater its affinity for the diluent, i.e. the greater its solubility in non-polar solvents. Thus it follows from published data[158] that in those instances where the amine salt ($AmineHNO_3$) is more soluble in the diluent, the quantity required for dissolution of the insoluble salt $[AmineH]_2[Pu(NO_3)_6]$ is smaller; the quantity of amine salt required for solubilisation of the complex salt also decreases in diluents which are more effective solvents for the simple amine salt. The composition of the organic phase corresponding to the limiting solubility[158] corresponds to the solvates $[TOAH]_2[Pu(NO_3)_6]$‡ in nitromethane, $[TOAH]_2[Pu(NO_3)_6].4TOAHNO_3$ in xylene, and $[TOAH]_2[Pu(NO_3)_6].2TOAHNO_3$ in dibromomethane. In the polar nitromethane, the salt being extracted dissolves without solvation, but in the other diluents solvation by the amine salt increases with decrease in the solvent power of the diluent. Shmidt et al.[182] demonstrated the existence of a relationship between the degree of solvation of $[TOAH]_2[CoCl_4]$ by molecules of the amine salt TOAHCl and the degree of association of the latter in the diluent. In the opinion of these authors, the degree of association of the amine salt used as extractant does not change in many extraction systems when the amine salt forms extractable compounds with metal salts. Wilson's data also agree with this suggestion, since in nitromethane, in which tri-*n*-octylammonium nitrate is monomeric, only two molecules of $TOAHNO_3$ take part in formation of the complex, whereas in xylene, in which the degree of association[68] of $TOAHNO_3$ is ~ 3, formation of the complex $[TOAH]_2[Pu(NO_3)_6].4TOAHNO_3$ involves the participation of three times the number of amine salt molecules, i.e. six molecules.

The solubilisation of extractable compounds by an excess of the extractant is a widespread phenomenon, which is observed not only in extraction with amine salts. The dissolution of salts of dibutyl hydrogen phosphate in non-polar diluents is possible only in the presence of an excess of this acid ester[189], i.e. when the molecules of the salt are solvated by molecules of the corresponding acid. The solubility of the solid salt is proportional to the concentration of acid in the solution raised to a power corresponding to the solvate number[189]. Thus in the dissolution of the solid salt, as a result of solvation by the corresponding acid, the law of mass action is observed in accordance with the stoichiometry of the solvate. In the solubilisation of liquid amine salts as far as complete dissolution of the salt, these stoichiometric relationships are not observed, since the solvate formed usually has a higher affinity for the amine salt phase; it remains in this phase and is not transferred to the non-polar phase until almost all the insoluble liquid amine salt is converted into a solvate soluble in the non-polar phase. Homogenisation of the two-phase liquid system takes place after addition of almost the

‡ TOA = $(n\text{-}C_8H_{17})_3N$ (Ed. of Translation).

total quantity of solubilising agent required for conversion of the polar phase into the solvate.

It should be noted that stoichiometric relationships between the solubilising agent and the amine salt, corresponding to the degree of solvation under the conditions of homogenisation, are observed only at relatively low concentrations of these substances in the non-polar solvents. At higher concentrations the quantity of solubilising agent required for the transfer of one mole of the insoluble salt into the medium of low polarity decreases[190], since solubility begins to be affected not only by solvation but also by the overall increase in the dielectric constant of the solvent occurring in the presence of the solubilising agent, which is usually a more or less polar substance. Increase in the dielectric constant of the medium, as noted in Section III, leads to a decrease in the association of the molecules of the amine salts and hence to an increase in their solubility.

V. THE INFLUENCE OF NON-SOLVATING DILUENTS ON THE EXTRACTION PROPERTIES OF AMINE SALTS

The influence of non-solvating diluents on extraction has been relatively little studied. In the early work on this problem, attempts were made to establish a relationship between the partition coefficients or extraction constants and the dielectric constant of the medium or the polarisability of the diluent[191-197]. Because of the strong influence of factors additional to those studied by the authors cited, unambiguous relationships could not be established in most instances. More fruitful work has been carried out in recent years by Rozen and Khorkhorina[198], based on the molecular theory of solutions, and also by Siekierski[185,199-203] and Vdovenko et al.[204], who based their conclusions on the theory of regular solutions and used the parameters δ for the extractants, diluents, and extractable complexes to take account of the influence of the diluents.

The position of equilibrium for a reaction in solution (including extraction) and the solubility of the reactants are determined to a considerable extent by the same thermodynamic functions. Thus the higher solubility of a given substance corresponds to a decrease in its activity coefficient in solution[45]. The decrease in the activity coefficient of an amine salt dissolved in a diluent also corresponds to a decrease in its extraction properties. At the same time it is evident that a decrease in the activity coefficient of a reaction product, e.g. the compound being extracted, leads to a displacement of the equilibrium towards formation of this compound[119]. As early as 1938 Hildebrand[119], pointing out the relationship between the position of equilibrium for reactions and the values of δ for the reactants, wrote: "In general we may summarise by saying that in order to get a large amount of a certain substance in an equilibrium reached in solution, one should employ a solvent which is a good one for the substance desired and a poor one for the substance or substances on the other side of the equation of equilibrium. The quality of a solvent in this connection may be determined by any or all of the factors considered in connection with solubility in general, viz. polarity, chemical combination and internal pressure." The internal pressure, which is one of the chief factors determining solubility in non-polar solvents which do not react chemically with the solute and which obey the laws governing regular solutions, is given by the parameter δ. The influence of the values of δ on the extraction equilibrium can be seen by examining the simplest thermodynamic equations for extraction equilibria[202-204]. If the extraction of a metal salt (A) by an amine salt (E) takes place according to the equation

$$A_{aq} + n\,E_{org} \rightleftarrows A \cdot n\,E_{org} \equiv EC_{org},$$

where EC is the extractable compound of the salt A with the amine salt, the equilibrium constant for this reaction is given by the formula

$$K = \frac{[EC]\gamma_{EC}}{[A][E]^n \gamma_E^n \gamma_A}, \qquad (7)$$

where γ_{EC}, γ_E, and γ_A represent respectively the activity coefficients of the compound being extracted, the extractant, and the extractable salt. If [EC] is the concentration of the element being extracted in the organic phase, and [A] its concentration in the aqueous phase, it follows from Eqn. (7) that the distribution constant for this element α at constant composition of the aqueous phase is given by the formula

$$\alpha = K'[E]^n \frac{\gamma_E^n}{\gamma_{EC}}. \qquad (8)$$

If the concentration of the extractant also remains constant, we have

$$\alpha = K'' \frac{\gamma_E^n}{\gamma_{EC}}, \qquad (9)$$

where K'' is a constant.

It can be seen from formula (9) that, when the diluent is replaced at constant composition of the phases, the changes in α will depend on the changes in the ratio γ_E^n/γ_{EC}, for which Rozen[198] proposed the symbol *dil*. According to the theory of regular solutions[205], the activity coefficients of solutes are related to the solubility parameters by the expression

$$\ln \gamma_2 = \ln \frac{\varphi_2}{x_2} + \frac{V_2\varphi_1^2}{RT}(\delta_2 - \delta_1)^2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right), \qquad (10)$$

where the subscripts 2 and 1 relate to solute and solvent respectively (x_2 is the mole fraction of solute in the solution). Smulek[195] and Siekierski[199] showed that, in complete agreement with this equation, the activity coefficients of amine salts dissolved in various diluents decrease with increase in the value of δ for the diluent. By substituting in Eqn. (9) the activity coefficients of the extractant and the complex being extracted given by Eqn. (10), Vdovenko et al.[204] obtained the following equation relating the distribution constant of the metal being extracted α_M with the values of δ and the molar volumes V of the extractant, the diluent, and the compound being extracted

$$\lg \alpha = \text{const} + \frac{0.8686}{RT}(V_{EC}\delta_{EC} - nV_E\delta_E)\,\delta_{dilt} + 0.4343\,(nV_E - V_{EC})\left(\frac{\delta_{dilt}^2}{RT} - \frac{1}{V_{dilt}}\right), \qquad (11)$$

where the subscripts EC, E, and dilt denote quantities relating to the compound being extracted, the extractant, and the diluent respectively. Analysis of Eqn. (11) shows[204] that the dependence of α_M on δ_{dilt} for a constant value of V_{dilt} should in general pass through an extremal value. Differentiation of Eqn. (11) with respect to δ_{dilt} shows that the position of the extremal value is determined by the relationship

$$\delta_{dilt}^{extr} = \frac{V_{EC}\delta_{EC} - nV_E\delta_E}{V_{EC} - nV_E}. \qquad (12)$$

In the systems examined by Vdovenko and his coworkers[204] this extremal value was a maximum. It follows from

Eqn. (11) that the second derivative of $\lg \alpha$ with respect to δ_{dilt} is proportional to $nV_E - V_{EC}$, so that the extremal value may be a maximum when the molar volume of the compound being extracted is greater than the sum of the molar volumes of the molecules of extractant in the compound. In these instances, with diluents of low polarity and the lowest values of δ, increase in δ for the diluent should lead to an increase in the extractive power of the amine salt solution. In most extraction systems, however, such a relationship is not realised, and only a decrease in the extractive power of the salts takes place with increase in the value of δ for the diluent. It follows from Eqns. (11) and (12) that this may also be observed when $nV_E > V_{EC}$, i.e. when the dependence of $\lg \alpha$ on δ_{dilt} passes through a minimum. Such a relationship has been described for the extraction of metal salts by tri-(2,2,4-trimethylpentyl)ammonium chloride[206], for which the partition coefficients decrease with increase in the value of δ for the diluent (in the order—hexane > toluene > benzene) and for extraction by tri-n-octylammonium chloride[51,200-210] (decane > mesitylene > xylene > toluene > benzene) and tridodecylammonium nitrate (cyclohexane > xylene > benzene)[211]. An unambiguous prediction of the nature of the dependence of $\lg \alpha$ on δ_{dilt} obviously requires an estimate of the ratio of the values of V_{EC} and nV_E.

It follows from the foregoing that, when there is no significant specific solvation, the influence of a diluent on the extractive power of amine salts, like its influence on their solubility, can be estimated approximately on the basis of the theory of regular solutions, from the known values of δ for a wide range of solvents. A knowledge of the values of δ_E and δ_{EC} for a larger number of amine salts and extractable compounds is required for the most extensive verification and application of this approach to estimating the influence of solvents.

Another approach has recently been proposed, which makes it possible to predict quantitatively the influence of various diluents on extraction. It is based on the observed[207] linear relationships shown by the free energies of many extraction systems with different diluents. The existence of these relationships has made it possible to develop a scale of DE-values (diluent effects) by means of which extraction constants K can be calculated for extraction systems with different diluents, if the corresponding constants K_0 for systems with a standard diluent are known[207]. The calculation is carried out using the formula $\lg K = \lg K_0 + \rho DE$, where ρ is a coefficient which is constant for a series of extraction systems of constant composition with different diluents, and DE is a constant which depends only on the nature of the diluent. The results of the calculation show good agreement with the experimental data for a large number of systems.

VI. THE INFLUENCE OF SPECIFIC SOLVATION ON THE EXTRACTION PROPERTIES OF AMINE SALTS

All solvation interactions of a solvent or of added reagents with a substance to be dissolved, leading to solubilisation of the latter, produce a decrease in the activity of this substance in the solution§. For example, solvation of the anions of amine salts by alcohols, leading to an increase in the solubility of these salts, simultaneously produces a decrease in the effective concentration of the free amine salt in the extractant, i.e. a decrease in its thermodynamic activity. As noted in the preceding Section, the change in extractive power produced by a diluent depends on the ratio of the changes in the activity coefficients of the extractant and the compound being extracted. Thus a decrease in the distribution constant for an element when an alcohol or other solubilising agent is added to the extraction system will take place if the extractant—the amine salt—is more extensively solvated than the compound being extracted.

In the extraction of metal salts by amine salts, the volume of the anions of the compounds being extracted is usually much greater than the volume of the anions of the simple salts used as extractants. This leads to greater delocalisation of the negative charges on the anions of the compounds being extracted, diminishes their electron-donating power, and hence decreases their solvation by electron-acceptor molecules relative to the solvation of the anions of the extractant. Thus the addition of alcohols usually leads to a marked decrease in the extractive power of amine salts. The extraction of uranium(VI) and zinc by tri-n-octylamine from hydrochloric-acid solutions[51,160] is decreased considerably when octanol is added to the extractant. The extraction of nitric acid[213-215] and a number of quadrivalent actinide elements by amine nitrates from nitric-acid solutions[164,216], the extraction of many elements by amine chlorides from hydrochloric-acid solutions[163,217-220], and the extraction of uranium(IV) sulphate by amine sulphates from sulphuric-acid solutions[221] also decrease when alcohols and chloroform are added. A similar effect should be observed on the addition of other solubilising agents which are electron acceptors capable of solvating anions—organic acids, halogenated hydrocarbons, etc.

It should be noted that, in the extraction of metal salts, this action of solubilising agents is observed only when the metal concentrations are low compared with the concentration in the non-polar diluent of the dissolved amine salt used as extractant. If the concentration of metal salt in the organic phase is high, the partition coefficient may even be greater in the presence of solubilising agents than in their absence. This phenomenon is due to the fact that, when a diluent of low polarity does not contain a solubilising agent, a considerable proportion of the amine salt is used up not only in the formation but also in the solvation of the compound being extracted, as a result of which, with increase in the concentration of the latter, the concentration of the extractant decreases rapidly with a corresponding rapid decrease in the partition coefficient[182]. In the presence of an excess of solubilising agent, the molecules of the compound being extracted are solvated not by the extractant but by molecules of this solubilising agent, and this leads to a decrease in the consumption of extractant and to a slower decrease in the distribution constant with increase in the concentration of the compound being extracted. As a result, at high concentrations of the compound being extracted, the value of the distribution constant in the presence of the solubilising agent may be greater than that in the absence of the solubilising agent.

The energy of solvation of the anions of an amine salt by alcohols and other acidic substances depends on the

§ Some authors[212] therefore suggest that the term solubilisation should be taken to mean not only the solvent action of additives, but also any decrease in the activity of a dissolved substance in a homogeneous binary solution when a third component is added.

electron-donating power of these anions[5,61,222,223]. With decrease in the electron-donating power and the associated decrease in the solvation of the anions, the influence of solvating solvents is reduced[149,154,224]. Thus the influence of the addition of alcohols and chloroform on the extractive power of amine sulphates is less than its influence on that of the corresponding nitrates, and its influence is less on the properties of the salts of secondary amines than on those of the salts of tertiary amines[225,226].

In the extraction of acids by an anion-exchange mechanism, a solvating solvent may not influence the extraction equilibrium if the free energy of solvation of the anions of the compound being extracted differs from the hydration energy of these anions in the aqueous phase by an amount close to the corresponding difference for the anions of the amine salt used as extractant. Thus addition of the solvating solvent chloroform to the extractant does not decrease the distribution constants in the extraction of TcO_4^- by amine sulphates[227]. In the extraction of TcO_4^- by an amine nitrate, the addition of solvents which solvate the anions decreases the distribution constant of technetium[228], since the amine nitrate is solvated by the solvent molecules to a greater extent than is the sulphate[224,229,230].

As noted above, the solvation of anions is an acid–base interaction. On this basis, it has been suggested[51] that this solvation is also important for diluents which have extremely weak acidic properties, e.g. aromatic hydrocarbons. Study of the extraction of zinc by tri-n-octylammonium chloride from hydrochloric-acid solutions[51] has in fact shown that, when a series of aromatic diluents is used, the partition coefficients of zinc decrease to a greater extent the stronger the acidic (electrophilic) properties of the diluent.

When the solubilising agent solvates the cations of the amine salt, the result may be not only a decrease in the distribution constant of the metal salt, but also in some instances an increase in the distribution constant[5,51]. Decrease in the distribution constant for extraction by tertiary amines takes place for reasons which are the same as those for solvation of the anion. Solvation of both cations and anions of amine salts leads to a decrease in the association of their molecules. Change in the degree of association of the normal salts of tertiary amines[182] does not lead to a significant change in their extractive power. In contrast to this, with the salts of primary amines and to some extent secondary amines, and also with the acid salts of tertiary amines, change in the degree of association leads to a significant change in extractive power, since the association of these salts is due to the formation of intermolecular hydrogen bonds involving their anions, and this decreases considerably their extractive power. As noted in Section III, the presence of solubilising agents which solvate the cations leads to depolymerisation of the salts and also an increase in their polarity[5], and hence to a marked increase in their extractive power[51]. Nemodruk[231] observed a marked increase in the extractive power of a salt of the primary amine aniline in the presence of a ketone. An increase in the extractive power of dioctylamine was also observed[51] when 4-methylpentan-2-one was added to the diluent; this phenomenon was not observed when the ketone was added to the salts of tertiary amines. From these data it follows that a necessary condition for an understanding of the general features of the influence of solvating diluents on extraction is an investigation to determine which part of the molecule of the amine salt is solvated by molecules of the diluent.

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THE ELECTRONIC STRUCTURE AND PROPERTIES OF THE σ-BONDS IN THE MOLECULES OF ORGANIC COMPOUNDS

N. D. Sokolov

1. INTRODUCTION

The importance of σ-bonds in organic chemistry lies not only in the fact that most organic compounds do not contain other types of bond but also in the fact that σ-bonds form the framework of all molecules in general. Approximately 80% of the energy of formation of aromatic molecules corresponds to σ-bonds, their elastic properties are determined to a considerable extent by σ-electrons, most chemical reactions are accompanied by the rupture and formation of σ-bonds, in many instances the sign of the dipole moments is determined by the σ-electrons, etc.

It is often assumed that the σ-bonds in polyatomic molecules are localised and that their interaction can be neglected. This view is refuted by a large number of experimental facts, for example the dependence of the ionisation potential of alkanes on the length of the chain of σ-bonds, the dependence of the position of the electronic absorption bands in the optical spectra on the length of this chain, the non-additivity of the dipole moments of halogenated alkanes, the hyperfine structure of their nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectra, and many others.

From the viewpoint of quantum mechanics, strictly speaking, it cannot be assumed that the electronic wave functions in a molecule are localised on individual bonds or groups of bonds. Since the molecule is a single unit, the electronic wave functions should characterise the molecule as a whole. When the LCAO-MO† method is used, this means that the one-electron wave functions of the molecule ψ_i should be made up of linear combinations of the atomic orbitals φ_k of *all* the atoms in the molecule:

$$\psi_i = \sum_k c_{ik} \varphi_k. \qquad (1)$$

According to this formula generally speaking in the stationary state each electron has a finite probability of being found close to each atom in the molecule. The need to represent the molecular orbital in form (1) for molecules with saturated bonds was demonstrated by Walsh[1] in his interpretation of the electronic spectra of a number of simple molecules AB_2, ABC, AB_3, HAAH, H_2AB, etc. Starting from the delocalised molecular-orbital model, Walsh developed a method by which it was possible not only to interpret the spectrum but also to predict the geometry of the molecule in the ground and excited states and also the vibrational structure of the spectrum, to determine the selection rules and polarisation of the bands, etc. The need to use delocalised molecular orbitals of type (1) can be seen particularly clearly for symmetrical molecules.

† LCAO-MO = molecular orbital approximated by a linear combination of atomic orbitals.

The necessary requirement that the molecular wave function should exhibit the same symmetry elements as the molecule can in general be satisfied within the framework of the LCAO-MO method only by means of a linear combination containing the atomic orbitals of all the atoms‡.

The delocalised character of the molecular orbital does not in itself mean that changes or perturbations taking place in one part of the molecule will necessarily influence all other parts of the molecule. The transfer of an effect depends on the magnitude of the interatomic and (for saturated molecules) intra-atomic interactions. Within the framework of the LCAO-MO method, the interatomic interaction is characterised by the resonance integral between neighbouring atomic orbitals, which depends on their degree of overlap. For a conjugated chain of π-bonds, one atomic orbital from each atom appears in formula (1), and all the resonance integrals β are the same; each atom (except the end members) interacts to the same extent with two neighbours (Fig. 1*a*). For an unbranched chain of C–C σ-bonds (if for simplicity we neglect the C–H bonds), formula (1) contains two atomic orbitals from each atom (one from the terminal atoms); each atomic orbital "interacts" with two neighbouring atomic orbitals, but these interactions are different. For example, let us consider atomic orbital *2* (Fig. 1*b*). It interacts with atomic orbital *1* of the neighbouring atom; as before, we denote the corresponding resonance integral by the symbol β. On the other hand, atomic orbital *2* interacts with atomic orbital *3* belonging to the same atom; the corresponding resonance integral can be denoted by β', whose absolute magnitude is less than that of β.

If the ratio $m = \beta'/\beta$ were zero, the C–C bonds in the molecule would be strictly localised. All its properties would be additive; the influence of each atom would be transmitted only to neighbouring atoms. In actual fact $m \neq 0$, so that, strictly speaking, additivity of properties should not be observed in saturated chains. The magnitude of β' is approximately proportional to the splitting of the *s* and *p*-levels of the carbon atom (i.e. the energy of the transition $s^2p^2 \rightarrow sp^3$). From experimental data for alkane molecules it follows that $m = 0.34$ (see for example Klopman[3])§. The interaction of the σ-bonds, which is taken into account by the integral β', is called the inductive effect.

The interaction of σ-bonds depends not only on the intra-atomic integral β', but also on the resonance integral β'', characterising the overlap of two even or two odd atomic orbitals of the chain e.g. atomic orbitals *2–4* or *1–3* (Fig. 1). This integral is of the same order of magnitude as β'; for simplicity, however, the integral β'' is neglected.

The fact that $|\beta'| < |\beta|$ is one of the factors which makes σ-systems differ from π-conjugated systems. Another reason for this difference, as will be seen later, is that in an unbranched chain of σ-bonds there are two atomic orbitals for each atom, and not one, as in π-conjugated systems.

‡ A systematic treatment of molecules by the LCAO-MO method, taking account of all the atomic orbitals, was proposed by Hoffmann[2]. See also papers by Clementi[21]—cf. footnote on p. 964.

§ Calculations show that the energy and the distribution of electron density depend only on the absolute value of m (see for example Yoshimuzi[4]).

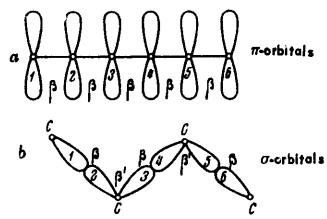


Fig. 1. Atomic orbitals: *a*) in chains of π-conjugated bonds ($m = 1$; $n = N$); *b*) in chains of σ-bonds ($m = 0.34$; $n = 2N - 2$).

2. ENERGY CHARACTERISTICS

Let us consider the simplest case, an unbranched chain of N linked atoms. For a chain molecule with conjugated π-bonds, we shall take account of only the π-electrons. Each atom will then have one p atomic orbital; the number of atomic orbitals n will therefore equal the number of atoms N. By setting up the molecular orbitals in form (1), substituting this expression in the Schrödinger equation, and solving the appropriate variational problem, we obtain n energy eigenvalues (see for example Streitwieser[5]):

$$\varepsilon_i' = \alpha + \lambda_i\beta, \; i = 1, 2, \ldots, n. \qquad (2)$$

Here α and β are the Coulombic and resonance integrals respectively, and λ_i the roots of the corresponding determinantal equation, which are different for different values of n. The solid lines in Fig. 2 show the arrangement of eigenvalues for different values of n; $\epsilon_i = \epsilon_i' - \alpha$. The upper and lower systems of levels (below and above the line $\epsilon = 0$) are fairly far apart for small values of n. The distance $\Delta\epsilon$ between the lower positive and upper negative levels (the so-called gap width), however, decreases with increase in n, and tends to zero as $n \rightarrow \infty$.

In a chain of σ-bonds, as noted above, we must take account of two types of integral, β and β'. Calculation[4,6,7] analogous to that carried out for π-systems gives for the energy the same formula (2), but now λ depends implicitly on m; as before, the number of molecular orbitals obtained is equal to the original number n of atomic orbitals, but now $n = 2N - 2$. If we assume the value $m = \beta'/\beta = 0.34$ indicated above, the energy levels obtained for different values of n will occupy the positions indicated by the broken lines in Fig. 2. The distances between energy levels with the same sign (+ or –) (Fig. 2) are much smaller than for conjugated systems ($m = 1$). Moreover, the gap width $\Delta\epsilon$ decreases with increase in n much more slowly than for π-conjugated systems, and as $n \rightarrow \infty$ it tends not to zero but to a finite value equal to 1.32β.

Fig. 2 shows the difference between the dependence on chain length of the total energy for π-conjugated bonds and for σ-bonds. In the approximation being considered, the total electronic energy is obtained if in each level, starting from the lowest, we place two electrons and take the sum of the energies of all the electrons. We then have $E = 2\sum_i \epsilon_i$. It is found that all the negative levels (number $n/2$) will be doubly occupied, and all the positive levels will be empty. If we now consider the energy corresponding to one bond (a pair of electrons), it can be seen from Fig. 2 that the absolute value of this quantity for $m = 1$ (solid lines) on going, for example, from $n = 2$ (ethylene) to $n = 4$ (butadiene) increases considerably, since the lowering of

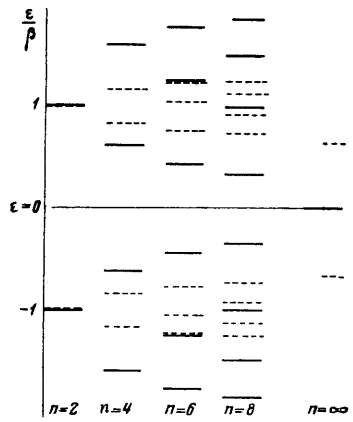


Fig.2. Energy levels for π-conjugated chains (solid lines) and for chains of σ-bonds (broken lines).

the lower level is much greater than the raising of the upper level. On the other hand, for $m = 0.34$ (broken lines) the lower and upper levels are displaced relative to the original level ($\epsilon = -1$) by approximately the same absolute amount, as a result of which the energy corresponding to each bond remains almost unchanged. For larger values of n the difference in these displacements is even smaller. This leads directly to the non-additivity of the energy for π-conjugated chains and, on the other hand, to the approximate additivity of the energy of formation of alkanes[8]; small deviations from this additivity are observed only for the first members of the homologous series.

From the foregoing it follows that additivity in energy of formation does not indicate localisation of electrons on bonds. As noted above, complete localisation would correspond to $m = 0$. Additivity in energy simply results from the mutual compensation of small effects of opposite sign.

The quantitative calculation of the deviations from additivity is much more complex, however. The molecular model chosen is too approximate to provide a basis for a calculation with the required accuracy, although many attempts have been made (e.g. for aromatic compounds[9] and alkanes[3,7,10]). Attention must first of all be drawn to the fact that the simplest version of the LCAO-MO method chosen (Hückel's method) does not give one of the fundamental properties of chemical bonds, their degree of saturation (see e.g. Ref. 11, pp. 146, 163, *et seq.*). This simplified scheme of calculation would indicate, for example, that the approach of two H_2 molecules should lead to the formation of a stable complex H_4, since the calculated energy decreases. In actual fact, on the approach of two H_2 molecules (or in general two covalent bonds A–B), the energy increases, and this indicates the saturated character of the bonds. This result is a consequence of the fact that in the simplest version of the molecular-orbital method the calculation is carried out with non-antisymmetrised functions, and no allowance is made for the interaction of the electrons with one another. Moreover, in a systematic calculation, all the bonds and all the electrons of the molecules must naturally be taken into account[12,13].

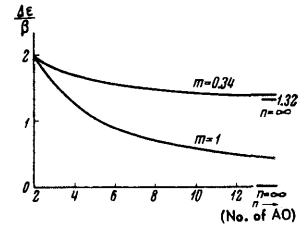


Fig.3. Dependence of the relative gap width ($\Delta\epsilon/\beta$) on the number of atomic orbitals (AO).

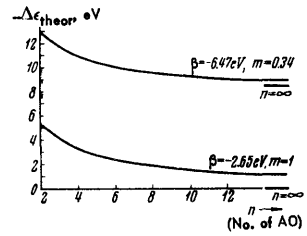


Fig.4. Dependence of the gap width ($\Delta\epsilon$) on the number of AO for $\beta_\pi = -2.65$ eV and $m = 1$ (lower curve) and for $\beta_\sigma = -6.47$ eV and $m = 0.34$ (upper curve).

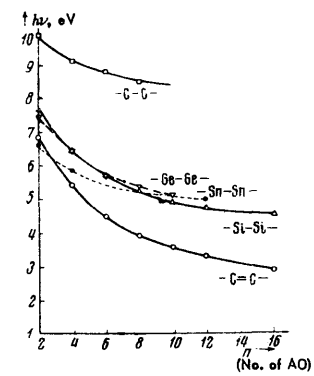


Fig.5. Experimental dependence of the absorption frequency on the length of the molecular chain[15].

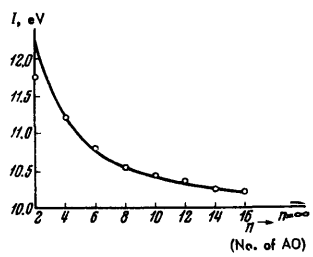


Fig.6. Dependence of the ionisation potential on the number of AO in the alkane chain.

The problem of calculating the non-additivity of energy is most clearly formulated when we compare the energies of two isoelectronic and isomeric molecules, one of which has conjugated π-bonds while the other has not. Thus, for example, for the two isomeric molecules

(A) $H_2C=CH—CH_2—CH=CH_2$ (penta-1,4-diene)
(B) $H_3C—CH=CH—CH=CH_2$ (penta-1,3-diene)

the latter has 6 kcal less energy than the former; this is usually attributed to the conjugation of the two π-bonds. In actual fact, however, this difference in energies results from the algebraic summation and partial compensation of a number of effects (by itself, the approach of the two π-bonds on going from A to B leads not to a decrease but to an increase in energy!). Thus, for example, the number of C–H bonds formed by carbon atoms having sp^2 hybridisation is six for molecule A and five for molecule B; the energies of these bonds may differ by 10–20 kcal. Analogous differences are observed in the energies of rupture of C–C bonds, in the energies of the interaction of different σ-bonds with one another and with π-bonds, etc. It is only when allowance is made for all these differences that we can hope to obtain a correct explanation [13] for the above decrease in energy on going from A to B.

Our initial simple model is adequate, however, for a semi-quantitative explanation of a number of the properties of molecules, e.g. the energy of electronic absorption. Within the framework of this model, the long-wave absorption band should correspond to a transition from the upper occupied level to the lower empty level, the distance between which is equal to the gap width $\Delta\epsilon$.

This quantity should be directly equated to $h\nu$, where ν is the frequency of the transition. Fig. 3 shows the calculated dependence of the quantity $\Delta\epsilon/\beta$ on n for a chain of π-conjugated bonds ($m = 1$) and for a chain of σ-bonds ($m = 0.34$). The quantity $\Delta\epsilon/\beta$ decreases much more slowly in the second instance than in the first. It should however be remembered that the resonance integrals for π-bonds (β_π) are smaller than those for σ-bonds (β_σ). Thus for the values $\beta_\pi = -2.65$ eV and $\beta_\sigma = -6.47$ eV adopted by Pople and Santry [14], for example, we obtain for $\Delta\epsilon$ the curves shown in Fig. 4. The similarity between these curves is greater than for identical values of β.

Fig. 5 gives experimental curves showing the dependence of $h\nu$ on n for polyenes (–C=C–), alkanes (–C–C–), and various other chain molecules containing σ-bonds (–Ge–Ge–, –Sn–Sn–, and –Si–Si–) according to published data [15]. The nature of the dependence of $h\nu$ on n is analogous to that expected on the basis of the model being considered. In each instance values of m and β can be selected which make it possible to reproduce these curves approximately by calculating $\Delta\epsilon$. The steep descent of the curve for the chain of silicon atoms apparently indicates that the corresponding integral β' has a comparatively large absolute value.

According to these calculations, the significant difference between the electronic spectra of polyenes and linear molecules having σ-bonds lies in the nature of the $\nu(n)$ relationships at large values of n. As noted above, as $n \to \infty$ within the framework of our model, the gap width in polyenes ($\Delta\epsilon_\pi$) tends to zero, whereas for chains of σ-bonds ($\Delta\epsilon_\sigma$) it tends to a finite limit of the same order of magnitude as β. This last feature is a direct consequence of the fact that $\beta' \neq \beta$. If we had $\beta' = \beta$, then $\Delta\epsilon_\sigma$ would also tend to zero as $n \to \infty$.

Our model, however, greatly simplifies the situation for polyenes with large values of n. Here effects which go beyond the scope of the model begin to play a part. Thus it is possible that alternation of bond lengths begins at large values of n in polyenes, yielding two different resonance integrals for adjacent bonds [16]; it can be seen from the foregoing that in such a situation the gap width does not tend to zero. Moreover, when $\Delta\epsilon$ is sufficiently small, the spacing between the electronic levels reaches the same order of magnitude as the vibrational quanta, so that the electronic and vibrational motion, strictly speaking, can no longer be considered independently. Moreover, with long chains there may be very significant interaction between the electrons [17,18]. This factor is apparently the most significant.

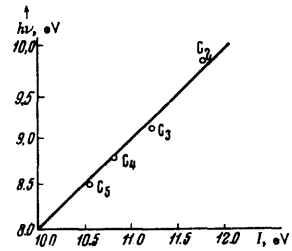


Fig. 7. Relationship between ionisation potential and absorption frequency.

The ionisation potential of a molecule in this model is simply equal to the energy (with opposite sign) of the upper filled orbital, for which $i = n/2$ in formula (2):

$$-I = \varepsilon_{n/2} = \alpha + \lambda_{n/2}\beta. \qquad (3)$$

Fukui and his coworkers [10] showed that, with $\alpha = -5.85$ eV, $\beta = -6.36$, and $m = 0.34$, good agreement is observed between the calculated and experimental values of I (with the exception of ethane, Fig. 6).

Since both the frequency of absorption and the ionisation potential are linearly dependent on $\lambda_{n/2}$, we should expect a linear relationship between these quantities, and this is confirmed for the alkanes (Fig. 7). For other classes of compound there are insufficient published experimental data to enable us to make a similar comparison of ν and I.

3. ELECTRON DENSITY DISTRIBUTION AND DELOCALISATION

The distribution of electronic charge in conjugated systems exhibits characteristic features, resulting from the delocalisation of the π-electrons. The most remarkable feature is that, under the influence of a substituent or a heteroatom, the electron density distribution changes throughout the conjugated chain, and alternation of charge is observed. This involves the alternation of the charges of the atoms with respect to sign or magnitude.

The charges q on the atoms in a polyene chain XC_5 (where X represents e.g. a halogen atom) are given in Fig. 8 (broken line) [6]. The "amplitude" of the alternation falls off very slowly with increasing distance from X. This alternation of the charges of the atoms does not take place in alkane chains XC_5 (solid line in Fig. 8). The positive charge produced on the C atoms by the substituent X decreases fairly rapidly to zero: it is almost equal to zero on the third atom from X [6¶].

¶ In Sandorfy's paper [6] the calculations for the σ-chains were carried out with $m = 0.25$.

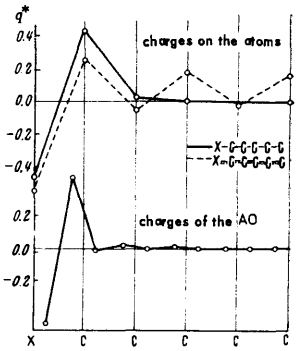


Fig. 8. Upper—charges on the atoms in an XC_5 σ-chain (solid line) and an XC_5 π-conjugated chain (broken line); lower—"charges" of the atomic orbitals in an XC_5 σ-chain.

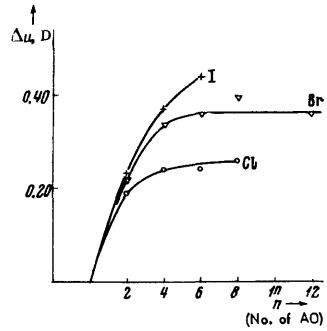


Fig. 9. Dependence of the difference in dipole moments $\Delta\mu = \mu(XC_NH_{2N+1}) - \mu(XCH_3)$ on the number of atomic orbitals [4].

It may be noted that, if we were speaking of the charges not on the atoms but corresponding to individual atomic orbitals (for polyenes these concepts are the same), we would find rapidly damped alternation for the latter in a chain of σ-bonds [6] (Fig. 8). The alternation disappears on passing to the charges on the atoms, since in order to obtain the latter it is necessary to sum the charges of the two atomic orbitals of each atom. Even if $m = 1$, alternation of the charges on the atoms would not take place in a chain of σ-bonds in which each atom had two atomic orbitals.

Calculation [19] has shown that the negative charge on the halogen atom X in halogenoalkanes XR increases with increasing length of the hydrocarbon radical R, as a direct consequence of the delocalisation of electrons along the chain of bonds. Thus an effect familiar in chemistry is obtained even with a simplified model which does not take account of the hydrogen atoms. It is found [19] that this increase in charge is accompanied by a simultaneous increase in the rate of nucleophilic substitution. Table 1 gives as example values of the charge q^* on the Br atom and of the relative rates of the reaction

$$RX + OH^- \rightarrow OH + X^-$$

for a number of normal alkanes and isoalkanes.

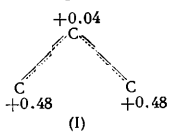
Knowing the charges of the atomic orbitals of a chain of σ-bonds and assuming that they are situated at the "centres of gravity" of these atomic orbitals, we can calculate the dipole moments of substituted alkanes [4]. Since the positive charge produced on the alkane radical under the influence of an electronegative substituent X is not localised on the single carbon atom nearest to X, the dipole moments are non-additive. The dependence of the difference $\Delta\mu = \mu(XC_NH_{2N+1}) - \mu(XCH_3)$ on the number of atomic orbitals is shown in Fig. 9. [4] The theoretical curves were calculated for $m = 0.34$. The dipole moment becomes constant at $n \geq 6$ (Fig. 9), i.e. beginning approximately at substituted propanes. Thus the delocalised character of the electrons in monosubstituted halogenoalkanes apparently has a significant influence on the charge distribution over not more than three atoms of the σ-chain.

TABLE 1. Charges on the Br atom and relative reaction rates.

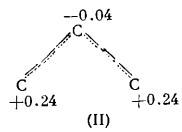
RBr	q^*	Relative rate of reaction $RX + OH^- \rightarrow ROX + X^-$	RBr	q^*	Relative rate of reaction $RX+OH^- \rightarrow ROX+X^-$
C–Br	0.423	1		0.467	10^8
C–C–Br	0.436	1.7			
C–C–C–Br	0.440	—			
	0 444	45		0.487	—

The example of the halogenoalkanes shows that the dipole moments of the σ-framework μ_σ may lead to non-additivity of the dipole moments for molecules having conjugated π-bonds. Allowance must be made for the fact that the value of β' is about 30% greater for sp^2 hybridisation than for sp^3 hybridisation. In general, μ_σ and μ_π are of the same order of magnitude; in some instances μ_σ may even exceed μ_π (for example, according to Berthod and Pullman [20], for pyridine $\mu_\sigma = 1.44$ D, $\mu_\pi = 0.86$ D, and $\mu_{exp} = 2.23$ D).

The change in the calculated charge distribution in a molecule containing π-bonds, occurring when allowance is made for the σ-electrons, can be assessed from the example of the allyl cation [2]. The electron density distribution represented in scheme (I) was calculated in the π-electron approximation without allowance for the C–H bonds. Scheme (II) gives the charges on the carbon atoms of the same cation, determined with allowance for both the π-electrons and the σ-electrons. It is found that the sign of the charge on the central carbon atom has changed, and that the magnitude of the charges on the terminal carbon atoms has decreased considerably, owing to the appearance of positive charges on the hydrogen atoms†.



(I)



(II)

† E. Clementi (U.S.A.) reported at the International Symposium on Quantum Chemistry in Kutna Hora, Czechoslovakia (1967), that, according to his calculations for polyatomic molecules, carried out in the self-consistent field approximation with allowance for all the electrons and integrals, the calculated electron density distribution of conjugated systems changes considerably when allowance is made for σ-electrons. Some of this work by Clementi has been published in the Journal of Chemical Physics [21].

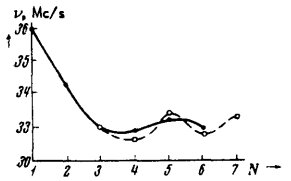


Fig. 10. Dependence of the n.q.r. frequency of the Cl atoms in compounds $Cl-[CH_2]_N-Cl$ on N (solid line—experimental, broken line—calculated).

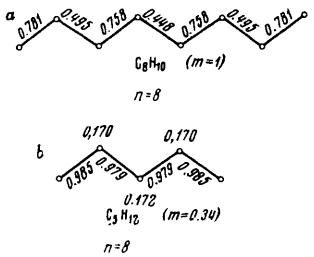


Fig. 11. Bond orders:
a) in a π-conjugated chain for $n = 8$ ($m = 1$);
b) in the chain of σ-bonds for $n = 8$ ($m = 0.34$).

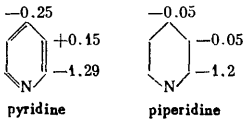
With symmetrical αω-dihalogenoalkanes the situation is apparently slightly different from that with monosubstituted alkanes. Calculations carried out by the molecular-orbital method for $m = 0.34$ show that the effective (negative) charge on the chlorine atoms in molecules of the type $Cl-[CH_2]_N-Cl$ show a characteristic dependence on the number N of CH_2 groups. When $N > 3$, the charges on the chlorine atoms vary periodically with increase in N: they are slightly greater for even values of N than for odd values, the difference amounting to 0.005–0.01 of a unit charge for the calculated examples with $N = 3$–7. This effect is apparently manifested in the nuclear quadrupole resonance (n.q.r.) spectra [22]. According to the calculations, the n.q.r. frequency of the chlorine atoms in these molecules is smaller for $N = 4$ than for $N = 3$ or 5 (Fig. 10). For $N > 5$ the dependence of the n.q.r. frequency on N is apparently more complex.

As with π-conjugated systems, it is possible to calculate the bond orders $p_{\mu\nu}$ for alkane molecules. A corresponding value of $p_{\mu\nu}$ is obtained for each pair of neighbouring atomic orbitals. For conjugated systems the values of $p_{\mu\nu}$ alternate along the chain of carbon atoms. The values of $p_{\mu\nu}$ for octatriene are given in Fig. 11*a*. Many conjugated systems show parallel changes in the bond orders, bond lengths, and force constants (see for example Streitwieser [5]). According to Konarski's calculations [23] the alternation of $p_{\mu\nu}$ is even more marked for a chain of σ-bonds (Fig. 11*b*); the low values of $p_{\mu\nu}$, however, are due to the intra-atomic interaction, characterised by the integral β'. Thus there is almost no alternation in the orders of real bonds in saturated hydrocarbons. On this basis it may be expected that these compounds should show alternation neither of bond lengths nor of force constants.

4. MAGNETIC RESONANCE SPECTRA AND DELOCALISATION

The experimental data on chemical shifts in n.m.r. spectra occurring when a substituent or a heteroatom is introduced into a molecule indicate that their influence is transmitted for a fairly large distance along a chain of either π-bonds or σ-bonds.

This influence, associated with delocalisation of electrons, resembles slightly the influence of substituents and heteroatoms on electron density distribution, but it does not reduce to this. The magnetic screening of nuclei is due to the precession of electrons in the external magnetic field, and in general it depends in a complex fashion on the properties of the molecule. Measurements of the proton chemical shifts σ_H and calculations of the π-electron charges for a number of nitrogen-containing aromatic compounds [24] showed that the discrepancy between the experimentally observed values of σ_H and the values calculated from data on the π-charge distribution is large: it may amount to 100–250% and have either sign. This comparison, it is true, made no allowance for the fact that not only the π-electrons, but also the σ-electrons, are in fact responsible for the chemical shift. The contribution made by the σ-electrons of the molecular framework is apparently fairly large. This follows, for example, from a comparison of σ_H for pyridine and piperidine [24]. The proton chemical shifts given below were measured relative to benzene and cyclohexane respectively.



As in the production of charges by induction, the influence of the perturbation on the atoms joined by σ-bonds is rapidly damped, and, in contrast to π-conjugated systems, the values of σ_H do not show alternation.

One consequence of electron delocalisation in aromatic compounds is the displacement of the n.m.r. signal from the protons towards weaker fields under the influence of the magnetic field of the "ring current". A similar effect, of small magnitude, is apparently observed with cyclic saturated hydrocarbons. For example, the equatorial hydrogen atoms in cyclohexane give an n.m.r. signal which is displaced slightly towards weaker fields relative to the signal from the axial protons [25]. The possibility of the production of ring currents in rings with alternation in the magnitude of the resonance integral was examined by London [26] in connection with the theory of the anisotropy of diamagnetic susceptibility in aromatic compounds. He concluded that the magnitude of the ring current is proportional to $(\beta'/\beta)_{n/2}$, i.e. that it is comparatively small.

The indirect spin–spin coupling of nuclei, taking place through the electron clouds separating them, is one of the most striking manifestations of the delocalisation of electrons through a system of σ-bonds. This coupling is due to "magnetic polarisation" of the electron cloud by the magnetic field of the nuclei. This polarisation can readily be imagined if we start from the picture of two-electron bonds interacting with one another. The magnetic field of the nucleus leads to partial (very small) "unpairing" of the spins of the pair of electrons in direct contact with this nucleus. The electronic magnetic moment produced in this way in turn produces a magnetic moment in the electron

pair of the neighbouring bond (as a result of the interaction of the bonds), etc.; the induced magnetic moment of one of the electron pairs interacts with the second nucleus and thus leads to magnetic interaction of the nuclei with one another. If the interaction (β') between the bonds, examined above, did not take place, indirect spin–spin coupling would not exist.

The energy of the spin–spin coupling is

$$W = K_{HH} I_1 I_2, \qquad (4)$$

where I_1 and I_2 are the spin moments of the first and second nuclei respectively, and K_{HH} is the so-called spin–spin coupling constant. Some values of K_{HH} for hydrogen and fluorine nuclei are given in Table 2.

These data show that conjugation does not always lead to an increase in K_{HH} (examples 5–7 in Table 2). The dependence of the absolute magnitude and sign of K_{HH} on the length of the chain of bonds and on the structure is apparently fairly complex. It is possible that in some instances, the curvature of a long chain allows the terminal atoms to interact directly with one another.

The simplest example is provided by the interaction of geminal hydrogen atoms (i.e. hydrogen atoms attached to the same carbon atom). It has been established experimentally that for these atoms the constant K_{HH} increases (becomes less negative or more positive) when the H–C–H valency angle increases. Moreover, the introduction of an electronegative X atom in the α-position to the CH_2 group leads to an increase in K_{HH} (e.g. for ethylene $K_{HH} = +2.5$, and for formaldehyde $K_{HH} = +4.0$). These regular features can be explained qualitatively as follows [27].

Two mechanisms apparently exist for the interaction of geminal atoms. Firstly, the magnetic moment of the nucleus may induce a magnetic moment in the electron pair of the $CH^{(1)}$ bond; as a result of the difference in the signs of the gyromagnetic ratio of the proton and electron, the direction of this moment will be the same as that of the nucleus (Fig. 12*a*). The electronic moment of the $CH^{(1)}$ bond will in turn "polarise" the electron pair of the $CH^{(2)}$ bond, whose induced magnetic moment will interact with the second H nucleus. The moment of the latter (Fig. 12*a*) is antiparallel to the spin of $H^{(1)}$. In accordance with Eqn. (4), the energy W will be negative (i.e. have a minimum) for the condition $K_{HH} > 0$. Secondly, we may have a mechanism in which the magnetic moment of the proton $H^{(1)}$, as a result of contact with the electron pair of the $CH^{(2)}$ bond, directly induces a magnetic moment in this bond (Fig. 12*b*). Analogous arguments lead to the conclusion that in this instance the spins of the nuclei will be parallel, and K_{HH} will be negative.

TABLE 2. Spin–spin coupling constants.

No.	No. of bonds	Carbon framework of molecule	K_{HH}, c/s
1	2	H–C–H (methane)	−12.4
2	2	H–C–H (cyclopropane)	− 4.0
3	2	H–C–H (ethylene)	+ 2.5
4	4	H–C–C–C–H	7–13
5	4	H–C=C=C–H	6
6	5	H–C–C=C–C–H	+2.7
7	5	H–C=C–C–C–H	0.7–1.3
8	6	H–C≡C–C–C≡C–H	1.3
9	7	H–C–C=C–C=C–C–H	1.0
10	5	F–C$_6$H$_4$–F	11
11	5	F–C–C–C–C–F	4.3
12	6	F–C–C–C–C–C–F	1.9

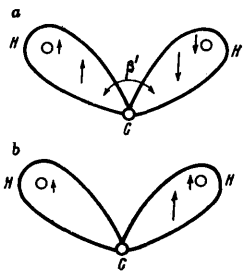


Fig. 12. Indirect magnetic interaction of geminal hydrogen atoms.

These two mechanisms compete with one another. The first is determined by the magnitude of the exchange integral β', which, as noted above, depends on the energy of the s–p splitting in the carbon atom, and the second is determined by the magnitude of the exchange integral between the atomic orbital of the $H^{(1)}$ atom and the atomic orbital of the carbon atom of the second bond. With increase in the s-character of the hydridisation of the carbon atom, the absolute magnitude of the integral β' increases [14] by 33%—$\beta'(sp^3) = -2.45$ eV, $\beta'(sp^2) = -3.27$ eV—whereas the absolute magnitude of the second integral decreases, because of the increase in the valency angle. Thus it is to be expected that K_{HH} will increase, i.e. will become more positive, and this is confirmed experimentally (see examples *1–3* in Table 2). The attachment of an electronegative atom X to the carbon atom will lead to a decrease in the population of the C–H orbitals and hence to a decrease in the negative contribution from the second mechanism: i.e. it will lead to an increase in K_{HH}.

A semi-quantitative treatment of these effects was put forward by Pople and Bothner-By [27]. There is as yet, however, no completely satisfactory theory of spin–spin coupling in molecules.

Electron delocalisation is revealed in e.s.r. spectra in the presence of a hyperfine structure from not one but several nuclei. The hyperfine structure of e.s.r. spectra is due chiefly to "contact" spin–spin coupling of the unpaired electron with protons or other nuclei having spins differing from zero. This interaction is possible as a result not only of the actual delocalisation of the unpaired electron but also of spin polarisation of the electron cloud, similar to the polarisation examined above, causing indirect spin–spin coupling of nuclei. It follows from the e.s.r. spectra of alkyl radicals [28,29] that the hyperfine structure is due not only to hydrogen atoms which are attached to α- and β-carbon atoms, but also to those on γ-carbon atoms. This means that in the e.s.r. spectra of these radicals the delocalised character of the unpaired electron influences atoms which are separated by three σ-bonds from the "mother" carbon atom‡.

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‡ The e.s.r. spectra show another extremely characteristic manifestation of delocalisation of the unpaired electron, which is observed in the spectra of organic radical-anions consisting of two aromatic rings joined by a bridging group. Here, however, the delocalisation does not take place through a chain of σ-bonds and is apparently due to π–σ conjugation, so that this effect lies beyond the scope of the present review [30–35] (the theory of the effect has been examined by a number of authors [36–38]).

This analysis of the electronic structure of molecules of saturated hydrocarbons confirms the view that in the theoretical examination of these molecules, as in π-conjugated systems, it is necessary to use delocalised molecular orbitals. The delocalised character of a molecular σ-orbital is reflected in the properties of the molecules much less strongly, however, than with a molecular π-orbital, as a consequence of the fact that, in contrast to π-conjugated systems, not all the resonance integrals in a chain of σ-bonds are equal. The intra-atomic resonance integral β', characterising the interaction of the σ-bonds, is smaller than the interatomic resonance integral β, responsible for the formation of the σ-bonds themselves.

The delocalised character of the σ-electrons is reflected to varying extents in different properties of saturated hydrocarbons. It has almost no influence on the energy of formation, which can therefore be calculated by an additive scheme. The delocalised character of the σ-electrons has a significant influence on the positions of the electronic absorption bands, the ionisation potentials, the electron density distributions, and in particular the dipole moments of the molecules. As a rule, however, the influence of electron delocalisation on these properties does not extend over more than 3–4 atoms in the chain of σ-bonds. It extends over a large number of atoms, for example, in the spin–spin coupling in n.m.r. spectra, because of the high sensitivity of nuclear magnetic radiospectroscopy.

The influence of delocalisation of σ-electrons is more marked in conjugated systems than in saturated molecules, since the intra-atomic exchange integral β' is 30% greater in these bonds than in saturated molecules. Thus, in the study of the transmission of the effect of structural changes along a chain of bonds in conjugated systems, it is necessary to make allowance not only for the part played by π-electrons but also for that played by σ-electrons.

The calculations of the properties of chains of σ-bonds given above are of course greatly simplified. They are based on the simplest version of the one-electron approximation, and a number of additional, strictly speaking unjustified, assumptions have been made. These include neglect of the integral β'' mentioned above, neglect of the C–H bonds, etc. In the treatment of comparatively simple properties such as the dependence of the ionisation potential on the length of the chain, appropriate refinements in the calculation would make it possible to obtain quantitative results, but should not alter significantly the qualitative picture obtained. For such complex properties as e.g. the spin–spin coupling of nuclei, however, comparatively extensive approximation is necessary in order to obtain even qualitative results. Thus the above interpretation of the indirect interaction of nuclear spins is based on more refined calculations than the treatment of the ionisation potentials or dipole moments.

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